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Method for Determining Potential Odor Contribution of Selected Kraft Process Streams

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The objective of this project was to define the potential odor contribution of selected process streams in the kraft industry that are routinely sewered. A procedure was suggested that can be used for this purpose.

Use of a dynamic olfactometer and odor panels to measure odor thresholds determined by complete volatilization of the sample or stripping of the sample were unsuccessful. No correlation between odor threshold and reduced sulfur concentration in the gas stream as measured by gas chromatographic techniques could be obtained.

Odor panels were employed using the head space analysis and the forced-choice triangle technique. It was shown that identifiable odor threshold values were more reproducible and judged more meaningful than simple odor threshold values.

It was shown that independent of mixing techniques, odor intensities of kraft mill process streams were additive. This was demonstrated for an acid sewer containing first chlorination stage effluent, digester condensates, and multiple-effect evaporator condensates; and for a total mill effluent with multiple-effect evaporator condensates, decker water, and odor-free dilution water used as make-up.

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METHOD FOR DETERMINING POTENTIAL ODOR CONTRIBUTION OF SELECTED KRAFT PROCESS STREAMS

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory-Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

The subject of this report is to define the potential odor contribution of selected kraft process streams that can be routinely sewered. During the course of this study a method was developed for determining the identifiable odor threshold of liquid samples which appears to have utility in problem analysis at the mill level. The potential odor contribution of effluent treatment systems was identified as a concern in the development of total reduced sulfur emission standards for new sources in the kraft industry. Before decisions can be made regarding the use of information generated in this study, some maximum acceptable level for these odors should be established. The benefits of reducing the odor threshold level of individual process effluents should be determined. If significant benefits are found, then the search for alternate control technology for replacement of the energy-intensive stripping procedures currently used should be initiated. For further information, please contact the Food and Wood Products Branch of the Industrial Environmental Research Laboratory, Cincinnati, Ohio.

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ABSTRACT

The objective of this project was to define the potential odor contribution of selected process streams and mixtures of liquid process streams in the kraft industry that are routinely sewered. A procedure was suggested that can be used for this purpose.

Use of a dynamic olfactometer and odor panels to measure odor thresholds determined by complete volatilization of the sample or stripping of the sample were unsuccessful. No correlation between odor threshold and reduced sulfur concentration in the gas stream as measured by gas chromatographic techniques could be obtained.

Odor panels were employed using the head space analysis and the forced-choice triangle technique. It was shown that identifiable odor threshold values were more reproducible and judged more meaningful than simple odor threshold values.

The group of process streams including white liquor, green liquor, black liquor, and weak wash all had high pH and sulfide concentrations. They yielded the highest identifiable odor thresholds of any other group of streams investigated with ED_{50} (effective dosage at 50 percent level) values varying from $<2.6 \times 10^6$ to 6.3×10^7. This emphasized the need to keep these in the process and to prevent their loss to the sewer. Condensate streams, including those from the multiple-effect evaporators, digesters, and the turpentine decanter underflow also had high ED_{50} values, ranging from 3.1×10^4 to $>1.4 \times 10^8$.

The identifiable odor threshold of the condensate stream to the steam strippers studied had a log average of 3.0×10^6 and the stripper product samples had an identifiable odor threshold of 1.4×10^4, a reduction in the odor level by a factor of about 200. These were in the same general range as the odor thresholds measured on biologically treated kraft mill effluents.

It was shown that independent of mixing techniques, odor intensities of kraft mill process streams were additive. This was demonstrated for an acid sewer containing first chlorination stage effluent, digester condensates, and multiple-effect evaporator condensates, and for a total mill effluent with multiple-

effect evaporator condensates, decker water, and odor-free dilution water used as make-up.

This report is submitted in fulfillment of Grant No. R-804646 by the National Council of the Paper Industry for Air and Stream Improvement, Inc. under the sponsorship of the U.S. Environmental Protection Agency. This work was performed during the period of July 20, 1976 to June 19, 1978.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

ASB	--aerated stabilization basin
b	--regression coefficient (y-intercept)
BSW	--brown stock washer
°C	--degrees centigrade
CFM	--cubic feet per minute
cm	--centimeter
comp.	--composite
cond.	--condensate, condensible
dec.	--decanter
dil.	--dilution
ED_{50}	--effective dosage at 50 percent level
elim.	--eliminator
evap.	--evaporator
FPD	--flame photometric detector
ft	--feet
gal	--gallon
GC	--gas chromatography
GLC	--gas-liquid chromatograph
ID	--inside diameter
ident.	--identification
l	--liter
lbs	--pounds
liq.	--liquor
m	--regression coefficient (slope)
m^3	--cubic meters
max.	--maximum
MEE	--multiple-effect evaporator
min.	--minute or minimum
ml	--milliliter
mm	--millimeter
NCASI	--National Council of the Paper Industry for Air and Stream Improvement, Inc.
no.	--number
NSSC	--neutral sulfite semi-chemical
OT	--odor threshold
panel.	--panelists
ppb	--parts per billion
ppm	--parts per million
ppt	--parts per trillion

Q_D --dilution air flow
Q_S --sample gas flow
r^2 --correlation coefficient
R_D --dilution ratio
SC --surface condenser
S_x --standard deviation of "x" values
S_y --standard deviation of "y" values
T --ton
TME --total mill effluent
US --United States

SYMBOLS

CH_3CH_2SH --ethyl mercaptan
CH_3SCH_3 --dimethyl sulfide
$[CH_3SCH_3]$--concentration of dimethyl sulfide
CH_3SH --methyl mercaptan
$[CH_3SH]$ --concentration of methyl mercaptan
CH_3SSCH_3 --dimethyl disulfide
$[CH_3SSCH_3]$--concentration of dimethyl disulfide
Cl_2 --chlorination
COS --carbonyl sulfide
H_2S --hydrogen sulfide
$[H_2S]$ --concentration of hydrogen sulfide
m --millimicron
$OT_{CH_3SCH_3}$ --odor threshold of dimethyl sulfide
OT_{CH_3SH} --odor threshold of methyl mercaptan
$OT_{CH_3SSCH_3}$--odor threshold of dimethyl disulfide
OT_{H_2S} --odor threshold of hydrogen sulfide
SO_2 --sulfur dioxide
Σ --summation
μl --microliter

SECTION 1

INTRODUCTION

The potential odor contribution of effluent treatment systems was identified as a concern in the development of total reduced sulfur emission standards for new sources in the kraft industry. Observations that have been made regarding the comparative odor level of feed and product of selected process streams that have been stripped for reduction of BOD contributing materials as an alternate means of reducing effluent load, let to consideration of requiring steam stripping of condensates as an integral part of these emission standards.

At that time several information gaps existed regarding the use of energy intensive measures such as stripping. Just how much odor could be tolerated from a biological treatment system had not yet been established. Perhaps the levels generated with BPCT treatment are adequate for most current situations. Certainly this was not the case where anerobic conditions existed in earlier forms of treatment. Neither was there any demonstrated evidence that any change in odor level in the vicinity of treatment plants occurs as the result of the use of strippers on process streams such as condensates from digestion and liquor concentration. This information gap still exists.

If, however, odor from liquid process streams is to be handled within the regulatory framework the energy use of practices such as stripping is intensive, and its general application to streams in a random manner without regard to their odor threshold is not practical. More extensive information regarding the odor contribution potential of individual process streams is required before sound engineering judgment can be made regarding (a) selective reuse of process streams within the operation as an odor control measure, and (b) the extent of stripping or other control technology applications can be defined which optimize energy use and effective odor control.

It was the objective of this project to define the odor threshold of selected process streams and mixtures of process streams that are routinely sewered. In carrying out the project, selection of suitable sample preparation and procedures for presentation of liquid samples to human panels for odor threshold measurements represented a significant effort and greater than initially envisioned. The method ultimately chosen relied on determination of an identifiable odor above a previously agitated sample in preference to definition of the detectable odor level which was not found suitable for an array of sample preparation methods. Chromatographic analysis for sulfur compounds in the liquid streams was also made to determine if this measurement could be correlated with the odor level determined by a panel of human observers. Information on odor threshold of selected process streams, components and mixtures of process streams was then generated.

SECTION 2

CONCLUSIONS

Three methods of sample preparation and two methods of sample presentation to panelists were investigated during the course of this study.

One sample preparation method involved suspension of a liquid sample in an air stream. Human observers were then used to determine the detectable odor level of the gas stream. There was not significant difference in the measured odor threshold of an array of effluent streams of divergent odor quality when using this procedure. These findings suggested that compounds were present in these streams which altered the detectable level of the presence of the liquid stream but which are not normally volatilized with the degree of turbulence encountered in sewers and treatment plants. The use of this sample preparation method was discontinued.

A second sample preparation method involved stripping of the liquid sample and measurement of the detectable odor level of the off-gas. Like the total volatilization method, there was no significant difference in detectable odor level of samples of divergent odor quality. The use of this sample preparation and presentation method was dropped for the same reasons that use of the total volatilization method was discontinued.

The method used for the bulk of the data generation was head space analysis of a sample agitated just prior to presentation to a panelist for identifiable odor threshold. Forced triangle procedures were used in making the panelists choice. This method differed in that the identifiable odor detection principle was used in contrast to use of the identification of a detectable change used in earlier portions of the investigation. Odor threshold values using this procedure were found to be reproducible and differed widely between streams of varying odor quality.

During the course of the investigation, information was generated on the odor threshold of the reduced sulfur compounds hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide. The odor threshold for these compounds was found to be generally consistent with those determined in recent years and reported in the literature. Variation in observed detectable level between individuals and from day to day for the same individual was evident, however.

No relationship between the level of reduced sulfur compounds in the liquid effluent samples and the detectable odor level using the total volatilization method could be determined.

The identifiable odor threshold of mixtures of kraft mill process streams was found to be calculable if the odor threshold of the component streams was known. The exceptions to this were mixtures where compounds of a mixture reacted, such as residual chlorine in first stage bleaching effluent with odorous compounds in other streams, resulting in a reduction in odor threshold.

The identifiable odor threshold of an array of process streams was generated. Those with the highest identifiable odor threshold were in-process streams not normally entering the sewers, such as white and green liquor.

Those condensate streams generated from digestion, multiple-effect evaporation of black liquor, and turpentine recovery were found to have high identifiable odor threshold levels. The actual level reflected the amount of dilution provided in the condensation step. Important in this phase of the study was the observation that the bulk of the odor in multiple-effect evaporator condensates is found in the condensates from evaporators containing the bulk of the BOD. These are the first liquor evaporation stages.

During the course of this study a method was developed for determining the identifiable odor threshold of liquid samples which appears to have utility in problem analysis at the mill level. It is likely that the odor threshold measurements using human panelists would have to be carried out away from the mill site. This is possible since odor threshold sample stability of stored samples was demonstrated. The findings of this study demonstrate that generic descriptions of process liquids are not generally adequate for problem definition for individual mill situations and their odor threshold level should be determined on a case by case basis.

SECTION 3

RECOMMENDATIONS

This study was concerned with only one element of at least a three-element information generation need. It dealt specifically with measurement of the odor threshold of process streams and effluents.

Before decisions can be made regarding the use of information generated in this study or that generated at individual mill sites, the benefits, if any, of reducing the odor threshold level of individual process effluents on odor generation at state-of-the-art effluent treatment plants should be determined.

If significant benefits are found, then the search for alternative control technology for replacement of the energy-intensive stripping procedures currently used should be initiated.

SECTION 4

LITERATURE REVIEW

ODOR REGULATIONS

Regulations that address odors and their control are general and elements of suitable regulatory approaches are frequently being reviewed. Historically, odor has been considered as a nuisance. Black's Law Dictionary defines a nuisance as:

> A class of wrongs that arise from the unreasonable, unwarrantable, or unlawful use by a person of his own property, either real or personal, or from his own improper, indecent, or unlawful personal conduct, working an obstruction or an injury to the right of another or of the public, and producing such material annoyance, inconvenience, discomfort, or hurt that the law will presume resulting damage. (1).

Cheremisinoff and Young (1) stated,

> Nuisance actions boil down to balancing the equities between property owners, each asserting his own rights to use his land. Factors that may be relevant in the case, however, include the availability of pollution control devices (2). Failure to keep pace with the technological advances in pollution controls (as was done by a competitor) resulted in a court ordering adoption of such controls. Of course, in any balancing of the equities the good faith efforts of the polluter, while not absolving him in any way, if they exist, would certainly be a factor if they were absent.

The nuisance theory approach is, in essence, that taken by the Texas Air Pollution Control Board for the regulation of emissions from odorous sources (3). Under this regulation, the mere presence in the atmosphere of an odorant is not considered as sufficient to prove a violation. The odor must be of such a concentration and of such duration so as to interfere with what is considered to be normal use and enjoyment of the quality of the property affected. Every effort is made to obtain a resolution on a voluntary basis. If this cannot be achieved, court action is taken.

The Bay Area Air Pollution Control District has adopted a finite procedure to establish whether or not an odor exists (4). The regulation incorporates several novel features. Prior to an action being taken, ten complaints must be received from ten individual complainants over a 90 day period. Samples are then collected of the emission itself or in the ambient air beyond the property line. The samples are presented to a panel of three judges using a dynamic olfactometer. Confirmation by two of the three panelists that an odor can still be perceived after appropriate dilution is an indication of violation of the regulation. Dilution of samples for analysis collected from an emission point is based on a predetermined factor based on stack height. Dilution of samples collected from the ambient beyond the property line is by a standard 4 to 1 ratio.

GENERAL PRECAUTIONS IN DETERMINING ODOR THRESHOLD

As will be noted in subsequent sections, there are certain general precautions that must be taken when utilizing either human odor panels to determine odor thresholds or instrumentation to estimate odor thresholds.

Two publications (5,6) discussed methods of measuring odors. The first article (5) discussed instrumentation, primarily gas chromatography, and the use of humans as detectors of odorous compounds emerging from a chromatographic column. The objective was to associate the odor with the chemical compounds responsible for causing the odor. This procedure was referred to as development of an odorgram.

The second article (6) discussed primarily human receptors in some depth. Odorgrams were mentioned, again utilizing human panelists to identify odors as they are eluted from a chromatographic column. In addition, the selection of odor panels was discussed. It was suggested that persons of low, high, and average sensitivity to odors all be represented on the panel. The concept of ED$_{50}$ (effective dosage at 50 percent level) was mentioned. This value represents that concentration at which 50 percent of the panelists could perceive the odor in the manner presented and 50 percent could not.

Duffee (7) stated:

> Not all of the problems of threshold determination are restricted to analytical inadequacies. Sensitivity to odorants varies widely, both within an individual from time to time and among different subjects. Exposure to suprathreshold odorant concentrations tends to lower olfactory sensitivity for that odorant. Also, odorants are usually mixtures of several compounds whose odors the nose tends to synthesize into a single response with an intensity that cannot be predicted from a simple

> addition of threshold values of the compounds. On the other hand, analytical instrumentation such as the GLC or infrared spectrophotometer tend to fractionate the mixture into its components. For these reasons it is not surprising that reported odor threshold values vary by as much as six orders of magnitude for the same compound, e.g., 5.1×10^{-1} ppm to 5.1×10^{-7} ppm for methyl mercaptan (8). Thus, we must rely on organoleptic techniques for most odor measurements."

One investigator indicated (9):

> The most logical approach to the determination of odor detection thresholds or 'odor units' associated with sources emitting complex mixtures of odorous gases is to evaluate the dose-response relationship of the source gas itself using human subjects, rather than to rely upon threshold data obtained from pure compounds or synthetic mixtures since neither of these two latter procedures will reproduce accurately the emitted odor quality of the several sources within the kraft process.

In the manual edited by Stern (10), it was reported to be difficult, if not impossible, to translate detection limits for single compounds prepared in a clean background to predicted odor detection thresholds in real world situations involving mixtures of both known and unidentified odorous compounds in a variety of background gases. The author questioned the use of synthetic mixtures of several gases because of the possible odor contribution from reported exotic sulfur containing cyclic or heterocyclic compounds in certain kraft process emissions.

CHARACTERISTICS OF ODOR

Definitions of Odor Characteristics

Huey (11) quoted the American Association of Heating, Refrigerating, and Air Conditioning Engineers Handbook of Fundamentals when he defined the sense of smell and odor as:

> The sense of smell is one of the five senses more or less involved in man's survival. The stimulus sensed (odor) has been used and is based incidentally or intentionally in the search for and enjoyment of food, to stimulate emotions, to judge the health or safety qualities of places, food, air and water. At appropriate concentrations, odors may be good or bad, that is to have a good or bad effect; at excessive concentrations, they are uniformly bad.
>
> Odorousness is defined as that property of a substance which excites the sense of smell. To be odorous, a

substance is usually in a gaseous or vapor state, or possesses a vapor pressure. Some odorants are pleasant, others unpleasant, depending on their psychological and sociological associations.

Odorants in themselves are not the cause of organic disease. The discomfort and disagreeableness that may be brought about by obnoxious odorants, however, may cause some temporary ill effects. The effects that fringe upon ill health include lowered appetite, lowered water consumption, impaired respiration, nausea, vomiting, and insomnia.

Odor was defined by Dravnieks (12) as four-dimensional, containing the characteristics of intensity, detectability, acceptability, and quality. Odor intensity was described by the mathematical equation:

$$I = kS^n$$

Where I = perceived intensity
S = intensity of the stimulus
k and n = numerical coefficients specific to the order.

The value of n tends to vary with the compound and ranges between 0.2 and 0.8 for sulfur gases. As an example, n-butanol has an $n = 0.63$, while the dimethyl sulfide n value is 0.48. There are indications that combinations of compounds exhibit smaller values of n than do single compounds. It further states:

> The human chemical sense cannot distinguish, by odor intensity, two concentrations of the same odorant if these concentrations differ by less than 15 to 30% (Weber-Fechner's law). For n-butylmercaptan and t-butylmercaptan, the differential threshold of 30% has been reported (13). Hence, an odorous effluent control which has reduced the odorous emission by only 15 to 30% will be barely observable even if the equally diluted 'before' and 'after' samples were available for a direct comparison, as long as the odor is still perceivable.
>
> The power law, applied, for example, to methyl sulfide with $n = 0.48$, indicated that a reduction by 75% (concentration to become 4 times lower) will reduce the odor intensity by only a factor of 2. If the intensity is still perceivable, such reduction is not evident to most observers by memory. Much more efficient reduction in the odorant emission is needed to produce a well-noticeable odor reduction effect, especially if odorants such as thiophenol and ethylsulfide, with even smaller n values, occur in the effluent.

Cheremisinoff and Young (1) characterized odors dealing with the phenomenon of human perception. They identified adaptation occurring when small changes in the environment affect behavior, indicating the changes can be pleasant or unpleasant, and that behavior modifications occur unconsciously to accommodate these changes when they are of minor nature. If an odor produces a certain stimuli of the sense of smell and the sensitivity of the sense of smell is reduced during the next stimulus of the same odor, adaptation has occurred, usually when smelling a single odor. If a second odor is introduced, adaptation will not be as severe as when smelling the single odor. Other terminology mentioned included anosmia, which is the loss of olfactory sensitivity, hyposmia, which is a partial loss of olfactory sensitivity and parosmia, which is a distorted olfactory perception, carsosmia if the distortions are unpleasant.

Relationship of Odor Characteristics to Perceived Odor

NCASI Atmospheric Quality Improvement Technical Bulletin No. 54 (12) was prepared by Dravnieks of the Illinois Institute of Technology Research Institute to provide a basis for the interpretation of odor panel findings derived from comparison of pre- and post-control process emission odor levels. The information presented on the relation between chemical composition and concentration, and odor level for a number of odorous sulfur compounds is particularly valuable in this respect. The extensive bibliography included in this report should prove useful to those endeavoring to improve their understanding of the fundamentals of this aspect of atmospheric pollution.

Cheremisinoff and Young (1) edited a book on odor which also contains an extensive bibliography on the subject. They reported on the work of Berglund, Berglund, and Lindvall (14) in which the principal of odor interaction was explored. The results indicated that the odor intensity of a mixture of odorous compounds was directly proportional to the arithmetic sum of individual intensities of the components. The concept presented suggested that individual odors are independent but that odor intensities are additive similar to light or sound intensities.

Cheremisinoff and Young concluded the following from additional work reported by Myddleton (1,15):

"1. Intensity of a mixture is about the same as the average of the component odors.
2. Pleasantness of a mixture is about the same as the average of the component odors.
3. Mixture nomenclature or response is the same as for single odorants.
4. No new qualities develop as a result of the mixture; that is the qualities of the mixture are determined by the qualities of the component odors. Note that

this is a contradiction of Bartley (16), where he finds that new characteristics may develop.

5. Berglund, Berglund, and Lindvall's work (14) confirmed by Myddleton, since he also found the characteristics of individual odors to be additive and to develop the new characteristics for the mixture.
6. Mixtures that involve three or four component odors do not become more complex olfactory experiences. We respond to mixtures in the same manner that we respond to single odors."

Summary

In summary, the characteristics of odor are as follows:

1. "That property of a substance which excites the sense of smell. To be odorous, a substance is usually in a gaseous or vapor state, or possesses a vapor pressure." (5)
2. Four-dimensional, with the characteristics of intensity, detectability, acceptability, and quality (6).
3. A reduction in odor concentration of 15 to 30 percent is barely observable as long as the odor is still perceivable (7).
4. It was reported (8) that the odor intensity of a mixture was the arithmetic sum of the components of the mixture.
5. The importance of adaptation was emphasized (1) suggesting that if an odor is not perceivable, it will not become perceivable by smelling for a longer period of time.

PHYSIOLOGICAL ASPECTS AFFECTING RESPONSE TO ODOR

Variables, other than dosage may effect response (17). Examples of such variables include the subject's age, sex, profession, attitudes toward air pollution in general or the source in question, and differences in earlier experience of related environmental events. It was also suggested that for practical and statistical reasons, the triangle test be utilized even though a simple yes-no scheme would allow more samples to be run over a set time period.

It has been reported (17) that the threshold of dimethyl sulfide and dimethyl disulfide when mixed together and determined empirically was about 70 percent of the calculated odor intensity. The conclusion arrived at was that an inhibitive or antagonistic effect existed. It was postulated that this may have been the result of some process at the perceptual level since the observation was particularly noticeable at lower concentrations.

Several articles and authors deal with the pleasantness and unpleasantness of the odor or odor hedonics (9,17,18). The latter article (18) presented detail on testing techniques and types of responses (pleasant vs. unpleasant) to be expected and how the data can be analyzed.

FACTORS FOR CONSIDERATION IN PANEL SELECTION

General Considerations

Duffee (7) discussed some of the pitfalls associated with the utilization of human odor panels. He stated that,

> Since people's reactions are so unreliable and variable, worst of all so expensive to secure, it is considered impracticable to depend solely on psychometric measurements. Instead, instruments must be developed that respond in a fashion similar to the human olfactory sense, but in olfactometry we are far from achieving the technical sophistication that is attained in audiometry or photometry.

However, he further stated,

> Although the human olfactory system does not compare in sensitivity to the chemical senses of many animals or insects, for most odorants, it does far surpass the detection limits of our analytical devices.

The literature does not delve into the matter of panel size other than generally stating, "the more the better," or if a small sample is used, then it should be selected to best simulate the norm. However, some investigators commented as follows (19):

> As previously indicated, all panelists are screened by the 'triangle' technique. Presently, neither the most sensative nor the most insensitive of those screened are being used, but those exhibiting average olfactory perception are selected.
>
> A sufficient number of screened panelists should be available so that the tests can always be conducted with a minimum of 6 panelists.

The same author (19) also made a list of items affecting panelist reliability judged by reproducibility of their results:

- Eating, drinking or smoking within 1 hour of panel.
- Insufficient sleep the previous night resulting in over-tired conditions.
- Personal behavior, i.e. a lack of interest or objectivity; easily influenced by others: inability to follow instructions, indecisiveness, etc.

- Use of personal odorants, such as colognes, perfumes, shaving lotions, etc. on day of panel determination.
- Impairment due to colds, hay fever, sinusitis, etc.
- Lack of training or experience in sniffing.

In the chapter of Young and Cheremisinoff written by T. M. Hellman (1) it was indicated that the response of an observer was dependent not only on the nature and strength of the stimulus but also on the degree of personal adaptation, motivation, attitude, expectancy, previous experience, and variation in background. Differences between observers due to age, health, sex, and smoking habits have been reported to influence olfactory sensitivity. However, investigations of these variables have generally produced contradictory and inconclusive results.

In determining the degree of detectability of an ambient odor or subjective annoyance, it was suggested that a balanced panel rather than a trained highly competent panel be used to best represent the community (12,17). This differs from the approach which would be taken in product quality control and research for the food and cosmetics industry (17).

Panel Screening Considerations

Cheremisinoff and Young (1) suggested that presecreening of individuals for the selection of panelists should be conducted with odorants similar to those to be perceived. It has been found that an individual's sensitivity to vanillin - methylsalicylate may not correlate with his sensitivity to sulfides or fatty acids. They also mention that background odors often hinder a determination and it may be necessary and appropriate to train the panelists to screen background odor from the determination.

They (1) also indicated that other than in a few simple cases, the chemical composition of odor is so complex and varied that the difficulties of a detailed analysis are nearly insurmountable.

Another discussion on the selection of panelists was presented by Duffee *et al*. (20). In the selection of an odor panel, care was stressed, as the members are chosen for their sensitivity, perceptual reproducibility, and experience. It was said that application of the triangle screening procedure using vanillin and methyl salicylate solutions in benzyl benzoate for the selection of odor panelists did not yield a consistent correlation between an individual's triangle test score and his relative sensitivity to industrial odors. This paper dealt with odor associated with the rendering, pulp and paper, and paint coating industries. They subsequently substituted methyl disulfide and butyric acid in a benzyl benzoate solution for the triangle tests. These latter results were found to have significant meaning with regard to the ranking of individual panelists.

ODOR PANEL MANAGEMENT

One investigator (9) indicated that screening of panelists and management of the program, including methodology, training, and motivation of the panelists, are important in developing reproducible results.

It was further reported (20) that panelists performed best in the forenoon hours. Just before and for at least two hours after lunch, their responses were quite erratic and on the low side by a factor of as much as three from their optimum. It was also noted that three hours panel duty seemed to be the effective span for obtaining panel results.

REPRODUCIBILITY OF INDIVIDUAL PANELIST RESPONSE

Another investigator (21) determined that the standard error of a particularly qualified observer could easily be ±40 percent on the same sample, whereas with a panel of four, the standard error could be reduced to ±20 percent on the same sample.

Still another article (9) indicated that a qualified panelist can have a deviation of 50 percent to the low side to 100 percent on the high side of a geometric mean concentration threshold. A further study (10) indicated that even though two observers may have nearly the same odor threshold for one compound (benzophenone), the same two individuals can differ by a factor of as much as five for another compound.

PRINCIPAL HUMAN ODOR MEASUREMENT TECHNIQUES

Duffee (17) identified four main categories of dilution-to-threshold measurement techniques which included:

"1. In-situ dynamic dilution (ISDD)--direct diversion of part of the odorous emissions or ambient air to the odor panelists on a continuous basis.
2. In-situ static dilution (ISSD)--direct diversion of discrete samples of odorous emissions or ambient air, to odor panelists housed in a static mixing chamber.
3. Off-site dynamic dilution (OSDD)--collection of discrete examples of odorous samples in suitable containers, transport to the odor panel, presentation to the odor panelists on a continuous basis.
4. Off-site static dilution (OSSD)--Same as 3 for collection and transport, but presentation to panelists in discrete parcels (e.g., syringe dilution)."

It is obvious that the ISDD technique has the least number of variables affecting the value derived, and thus should give the most reliable results since it eliminates the need for storage and/or transport of discrete samples of the odorous emissions.

Syringe

Much of the earlier odor panel work and even some of the more recent information have been developed utilizing the syringe dilution technique (19,22). This is a technique in which the panelists each receive a gas sample from the master syringe at a known dilution level introduced into their own syringe. The panelists then provide the last stage of dilution by drawing odor-free air into their syringe. A "yes-no" answer is obtained to determine the threshold level.

Blenders

One study (23) reported 30 panelists selected to represent a desired populace were used simultaneously. Odor meters (dynamic gas blenders) were used with the scale of concentrations being based on the fifth root of ten ($10^{0.2}$), i.e., a geometric progression having increments of about 59 percent.

Odor Rooms

Others (24) used different methods of measuring odor or odor thresholds. The panelists in this survey were in a static air system utilizing a "low odor" or virtually odor-free background air from an activated charcoal filter as the dilution medium. The odor threshold was defined, for this study, as the lowest level at which all the panelists could detect an odor. This was said to be consistent with the definition for minimum identifiable odor.

Olfactometer

Many types of instrumentation for the determination of odor thresholds are presented in the literature. However, the dynamic forced-choice, triangle olfactometer as developed and used by Dravnieks (5-29) seems to have maximum applicability when considering reproducibility, accuracy, and portability. One reference (26) indicated that one of its advantages, namely a large dilution range, may be a weakness since there appears to be a systematic error of 20 to 50 percent to the high side when an auxiliary 27:1 splitter is introduced to the system. The olfactometer is preferably used with 7 to 10 panelists. Each is forced to select one of the three sample ports which is different than the others, even if a guess is required. The results are analyzed statistically to derive the odor threshold.

Instrumental Analysis for Selected Odorous Compounds

The chemical analysis for odorous constituents is not a procedure that is widely practiced. The exception is the measurement of reduced sulfur compounds. Gas chromatography using a flame photometric detector is the most widespread application of this principle. The comments in this are therefore confined to this measurement procedure.

In two articles, Stevens (30,31) elaborated on various detection methods for sulfur gases, discussing the use of a 34 foot, 0.085 inch I.D. FEP Teflon^R tubing packed with polyphenyl ether five-ringed polymer containing phosphoric acid on 40/60 mesh Teflon^R column prior to a flame photometric detector.

Other articles (10,30-34) elaborated on the operation principles of the FPD and other methods of measuring sulfur gases such as coulometric detection, conductimetric detection, methylene blue with STRaction 10 (arabin ogalactin) wet chemical technique and the West-Gaeke colorimetric wet chemical technique. The use of a 394 m filter with the FPD was noted, yielding a specificity to sulfur over hydrocarbons of at least 10,000 to 1.

Several authors (35-39) relate instrumental response to varying concentrations of sulfur present in different compounds. However, some are related in peak height without actually giving an attenuation base, making it virtually impossible to determine a lower detection limit. One article (38) indicated that for the gases of prime interest (H_2S, CH_3SH, CH_3SCH_3), a minimum concentration of 11.5 to 24 ppb could be detected. Another author (37) indicated that by taking extreme measures, the detection limits for H_2S could be stretched to 7 ppb and to 15 ppb for CH_3SH. One additional author (40), using a wall-coated open tubular column made of borosilicate glass (30-38 m x 0.25 mm I.D.) and coated with OV-101 or SP-2100 was able to detect sulfur compounds at ppt levels when using a cyrogenic enrichment sampler. Good reproducibility was reported at the 5 ppb level without the enrichment sampler.

Two articles (41,42) discussed the use of permeation tubes for the calibration of flame photometric detectors. One author (42) elaborated on the use of an exponential dilution flask to obtain even lower levels of the sulfur gas for calibration through the entire range.

Columns for separating sulfur gases other than the previously mentioned polyphenyl ether column (Stevens column) (30), have also been mentioned in the literature. Bruner *et al.* (43) had success with a 0.4 cm I.D. by 80 cm Teflon^R column packed with 40/60 mesh Graphitized Carbon Black. They reported detection limits of 5 ppb for H_2S or SO_2 and 15 ppb for CH_3SH. However, for heavier sulfides the retention time becomes a factor on the limits of detectability. deSousa and Bhatia (44) reported on an acetone washed Porapak QS column that separated H_2S, COS, SO_2, CH_3SH, CH_3SCH and CH_3SSCH_3. The column was a 18.5 cm by 3 mm O.D. Teflon^R tube that had been acetone washed prior to filling with the acetone.

Another researcher (45) indicated that when measuring the reduced sulfur gases of interest at 0.2 to 0.8 ppm, columns constructed of 0.3 mm O.D. stainless steel tubing cleaned with benzene, chloroform, acetone, and distilled water followed by a rinse with 3 percent Siliclad solution and heated at 110°C for one hour were adequate. Several columns of 3 mm O.D. stainless steel tubing were then utilized following this procedure, including a 3 m 6 AW DMCS 80/100; 1.8 m column packed with specially treated silica gel (maybe deactagel); a 1.8 m column packed with 5% silicone QF 1-6500 on 80/100 mesh Porapak QS; and a 7.3 m column packed with 10% polyphenyl ether (6-ring) and 0.4% phosphoric acid on chromasorb G AW DMCS 80/100.

Two additional papers outlined the uses of various columns for sulfur gas analysis. The first (46) indicated the separation of H_2S, SO_2, and CH_3SH on Carbopak B-HT-100, the separation of COS, H_2S, CS_2, and SO_2 on Chromosil 310, the separation of H_2S, COS, SO_2, CH_3SH, CH_3CH_2SH and CH_3SCH_3 on Polyphenyl ether/Chromosorb T, and the separation of H_2S, COS, SO_2, CH_3SH, CH_3SCH_3 and CH_3SSCH_3 on Supelpak-S. In the second article (47) the use of a 40/60 mesh Chromasorb T column coated with 12% polyphenyl ether and 0.5% H_3PO_4, a Carbopak B-HT-100 column, a Chromasil 310 column, and a 120/140 mesh Deactagel column packed in 1 foot of 0.085 inch I.D. FEP Teflon^R were compared.

COMBINATIONS AND ALTERNATE ODOR ANALYSIS TECHNIQUES

Weurman (48) analyzed samples by more than one technique. He found that odor sensory dilution techniques utilizing humans and gas chromatography should be considered complementary to each other. A second investigator (49) reported that the ASTM syringe dilution technique did not correlate at all with either an odor room or dynamic dilution technique. Another approach reported was that of human odor identification of individual compounds at the exit of a gas chromatographic column. This is sometimes called an odorgram (50,51). It has proven to be beneficial for determining odor intensities of specific compounds as well as identifying them.

Cheremisinoff and Young (1) further stated,

> It is our opinion that the odor-in-water test is more reliable than the odor-in-air test. This may stem from the almost unlimited amount of sample to be sniffed from each dilution. The biggest difficulty with odor-in-water testing is obtaining odor-free dilution water. We have

on many occasions obtained positive responses from distilled water alone.

KRAFT MILL ODOR IDENTIFICATION AND THRESHOLD

Sarkanen, Hrutfiord, Johnson, and Gardner (52) indicated the primary constituents of kraft mill odor were the sulfide gases, hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and methyl mercaptan's oxidation product, dimethyl disulfide. This article stated that kraft mill odor will be very difficult to totally eliminiate or control because of two factors, (a) the very low odor threshold of the previously listed gases, and (b) the large number of sources from which odors emanate around a kraft mill. This article also contained a very complete bibliography of articles pertaining to kraft mill odor.

Several authors published information relating to the odor threshold of the reduced sulfur gases of interest in this project. This information is presented in Table 1.

TABLE 1. ODOR THRESHOLD OF VARIOUS REDUCED SULFUR GASES REPORTED IN THE RECENT LITERATURE

	Odor threshold (ppb)				
Investigator	H_2S	CH_3SH	CH_3SCH_3	CH_3SSCH_3	Method
Leonardos (24)	4.7* 0.47**	2.1	1		Minimum identifiable odor
Nishida (53)	39.5		26		Dynamic olfactometer,
	60		4.4		Syringe
	1		0.992		Triangle bag test
Polgar (54)	20				Dynamic dilution
Wilby (23)	4.1	0.80	2.1	5.6	Medians from dynamic mixing
	s.d.=2.9	s.d.=0.71	s.d.=2.2	s.d.=6.4	

* from Na_2S
** gas

Several investigators have reported in the literature published prior to 1968 odor threshold values for these same compounds. However, much of this work was performed prior to the development of what is considered current sample measurement and handling technology capability. The construction materials used in some of these early dilution systems suggest system losses may have influenced the results. Thus, these threshold values tend to be significantly higher than those currently reported. One of the better summaries of this work was compiled by Droege (55).

Limited work (56) indicated dilutions of 200,000 for flash and blowheat condensate, 35,000 for field treated condensate, and 2,000 for laboratory treated condensate were required to reduce the odor of these streams to threshold levels. The same report indicated that at another kraft mill, the accumulator condensate had an odor threshold at 240 dilutions whereas the steam stripped condensate had an odor threshold at 5 dilutions.

In a progress report on a CPAR project by Domtor (57) the following conclusions regarding kraft mill process streams were presented:

"(1) Although all the area sewers contained some odour, those from the kraft mill were, by far the most obnoxious

(2) (From Tables V and VI)* it may be seen that the kraft mill evaporator condensates and the kraft mill digester foul water condensate have the highest odour intensities and contributions and in total, constitute, practically speaking the whole odour contribution. These condensates fortunately represent only 7.6% of the total mill effluent volume.

(3) Minor contributions to the odour problem comes from the recovery furnace flue gas condensate, no. 9 seal tank effluent (Kraft Bleach Plant after the Hypochlorite Stage) and the Sulphite Mill Waste Liquor.

(4) Bench scale activated sludge and aerated lagoon experiments on various combinations of the indicated problem sources showed up to 99% reduction in relative odour contribution from a combination of the evaporator condensates and the digester foul water condensate, and only a slightly lower efficiency when including the recovery furnace flue gas condensate.

(5) Bench scale chemical oxidation/stripping by aeration gave between 95% and 98% reduction in the odour contribution of the same effluent combinations listed under (4).

(6) T.C.A. (Turbulent Contact Absorber), pilot plant oxidation/stripping by aeration gave 96% reduction in relative odour contribution of the same effluent combinations as above."

The potential for the evolution of odor from treatment systems and some methodology of removing the odor in a laboratory situation were discussed. Two articles (58,59) addressed the potential for evolution or stripping of organic compounds from

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* Reproduced as Tables 2 and 3 on the following pages.

TABLE 2. ODOUR AND TASTE THRESHOLDS* OF POINT SOURCES

Source	Area	A.P.H.A. odour threshold no. (1)	A.P.H.A taste threshold no. (2)
Evaporator condensate (seal tank)	Kraft mill - old recovery sewer	2,000,000	200,000
Digester foul water condensate	Kraft mill - main sewer	633,000	500,000
Evaporator condensate - (barometric well)	Kraft mill - old recovery sewer	41,600	500
Sulphite mill waste liquor	Sulfite mill - main sewer	25,000	142,800
#9 Seal tank (hypochlorite stage)	Kraft mill - bleach plant sewer	10,000	2,500
Recovery furnace flue gas condensate	Kraft mill - new recovery sewer	2,500	1,250
Vanillin plant barometric well	Vanillin plant - main sewer	1,430	10
Kraft mill west sewer	Kraft mill - main sewer	1,430	-
#11 Seal tank (unbleached pulp thickener)	Kraft mill - bleach plant sewer	910	250
Causticizing effluent	Kraft mill - old recovery sewer	830	500
Vanillin plant cooling water	Vanillin plant - main sewer	770	200
Kraft mill middle sewer	Kraft mill - main sewer	670	-
#8 Seal tank (chlorination stage)	Kraft mill - bleach plant sewer	590	170
Sherbrooke thickener	Sulphite mill - main sewer	290	1,430
#12 Seal tank (ClO_2 stage)	Kraft mill - bleach plant sewer	220	170
#1 Machine white water	Kraft mill - bleach plant sewer	40	-
White water chest	Sulphite mill - main sewer	-	6,670
Cowans rejects	Sulphite mill - main sewer	-	500
#10 Seal tank (ClO_2 stage)	Kraft bleach plant sewer	-	170
Bleached tertiary rejects	Sulphite mill - main sewer	-	30

* Thresholds are at 75% level.

1. Five day composites using detailed testing method.
2. One day composite using screening method.

TABLE 3. RELATIVE ODOUR AND TASTE CONTRIBUTIONS OF POINT SOURCES

Source	Area	Relative * odour contribution	Relative ** objectionableness of odour	Relative * taste contribution
Evaporator condensate (seal tank)	Kraft mill old recovery sewer	28,000	10	2,800
Digester foul water condensate	Kraft mill main sewer	6,330	9	5,500
Evaporator condensate (barometric well)	Kraft mill old recovery sewer	790	6	10
Recovery furnace flue gas condensate	Kraft mill new recovery sewer	180	4	90
Sulphite mill waste liquor	Sulphite mill main sewer	175	7	1,000
#9 Seal tank (hypochlorite stage)	Kraft mill bleach plant sewer	120	5	30
Kraft mill west sewer	Kraft mill main sewer	17	4	-
Vanillin plant (barometric well)	Vanillin plant main sewer	13	3	1
Causticizing effluent	Kraft mill old recovery sewer	12	2	7
#11 Seal tank (unbl. pulp thickener)	Kraft mill bleach plant	11	6	3
Sherbrooke thickener	Sulphite mill main sewer	9	6	44
Kraft mill middle sewer	Kraft mill - main sewer	3	4	-
#12 Seal tank (ClO_2 stage)	Kraft mill - bleach plant sewer	3	4	2
#1 Machine white water	Kraft mill - bleach plant sewer	3	3	-
Vanillin plant cooling water	Vanillin plant - main sewer	1	-	0.2
#8 Seal tank (chlorination stage)	Kraft mill - bleach plant sewer	1	4	2
Cowans rejects	Sulphite mill - main sewer	-	-	3
#10 Seal tank (ClO_2 stage)	Kraft mill - bleach plant	-	7	2
Bleached tertiary	Sulphite mill - main	-	3	0.1
Total mill effluent		(1,890)		(5,880)

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* Flow of sewer as percent of total mill flow divided by threshold concentration.

** Rated on a 1-10 scale using 6 and 7 paper machine sewer as "1" and seal tank new evaporators as "10".

biological treatment facilities. In the first article (58) the author discussed the calculated desorption of volatile gases and liquids from aerated stabilization basins using a mathematical model and certain fixed parameters. These parameters were controlled to determine their effect on the desorption rate. It was concluded that the most important parameters that affect stripping in aerated stabilization basins were temperature, wind velocity, liquid droplet diameter, and aerator interfacial area. The second publication (59) discussed a method of physically removing the volatiles from solution by simulating an aerated stabilization basin, and measuring the volatile organics removed.

It is recognized there are many additional references on odor and its measurement. The review selectively presents information in the literature of the last decade, several articles of which contain comprehensive bibliographies and in general represent the advances in odor measurement technology during that period.

SECTION 5

EXPERIMENTAL METHODS

During the course of this investigation three separate procedures were used in preparing samples for their presentation to human odor panelists. Two were discontinued since they were not found to be applicable in reaching the objectives of this study. The first involved total volatilization of a known volume of liquid sample into a known gas volume. This procedure was found not to be applicable since it was incapable of distinguishing between the total odor level of the sample and that portion which was readily volatilized with agitation at 40°C. Use of this procedure also produced odor thresholds which differed only slightly, if at all, between sources.

To overcome problems associated with the total volatilization procedure a stripping procedure was investigated. It was found to suffer some of the problems of the total volatilization method, namely inability to distinguish odor level between widely varying sources which were evident, even to the casual observer.

A head space analysis was ultimately used which incorporated the forced choice triangle test in conjunction with the procedures outlined in Standard Methods (60).

Each of these sample preparation procedures is described in the order they were used during the course of the study. The bulk of the data were developed using the head space analysis procedure, however.

SAMPLE COLLECTION AND STORAGE

The procedure for sample collection and storage was consistent during the course of this study. Samples to be analyzed were collected in 300 ml glass stoppered bottles and delivered to the NCASI West Coast Center where they were refrigerated overnight prior to odor analysis.

Samples collected from West Coast mills generally arrived at the West Coast Center on the same day they were collected, whereas samples from the Southeastern U.S. were in transit four to six days after collection. Storage of this duration was found to have an insignificant impact on the "identifiable" odor level.

HUMAN ODOR PANEL SELECTION

Panelists were initially selected on their ability to detect (a) the standard kraft pulping process reduced sulfur gases such as hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide and (b) n-butanol at or close to the literature reported values using a dynamic olfactometer. Panelists were screened on a regular basis and accepted or rejected on their continuing ability to detect the standard sulfur gases at or close to the detectable concentrations found in this study of 1.9 ppb hydrogen sulfide, 0.43 ppb methyl mercaptan, 3.3 ppb dimethyl sulfide and 0.80 ppb dimethyl disulfide. The purpose of the latter was to eliminate those panelists that had periodic extreme olfactory responses, either high or low. This was necessary to maintain an "average" sampling of olfactory responses. To qualify, the panelist had to be no more than a factor of three higher or lower than the threshold level. This variation was selected since the olfactometer had a factor of three difference between dilution stages. Thus, missing the correct concentration by one dilution stage would result in an error by an approximate factor of three.

SAMPLE PREPARATION FOR THE TOTAL VOLATILIZATION TECHNIQUE

A total odor or volatilization method involved the volatilization of about 0.1 ml of sample into 17 liters of clean, dry air. This was accomplished by placing a midget impinger with two side ports in a 100°C bath, and purging with charcoal filtered, desiccated air as shown in Figure 1. The air volume was measured by a wet test meter. A Teflon^{R} or Tedlar^{R} sample bag was connected to the outlet of the impinger and 0.1 l of sample was injected into the impinger.

SAMPLE PREPARATION FOR THE STRIPPING TECHNIQUE

The stripping technique for sample preparation was simpler in design. The principle was stripping at room temperature to remove the volatile compounds. This utilized a glass stripper column, 2.5 cm I.C., filled with glass beads and helixes to a height of about 30 to 35 cm, that received liquid sample at a flow of about three to five ml/min and utilized nitrogen as the stripping gas at a rate of about two l/min as shown in Figure 2. The flow of liquid sample to the column was controlled by the use of an orifice and constant head device. The gas handling sequence included a nitrogen cylinder, regulator, micrometering valve, wet test meter, desiccant, activated charcoal filter, stripping column, and a 17 liter Teflon^{R} or Tedlar^{R} bag. During the stripping process, temperature was measured by using a thermometer that had been placed in the column packing.

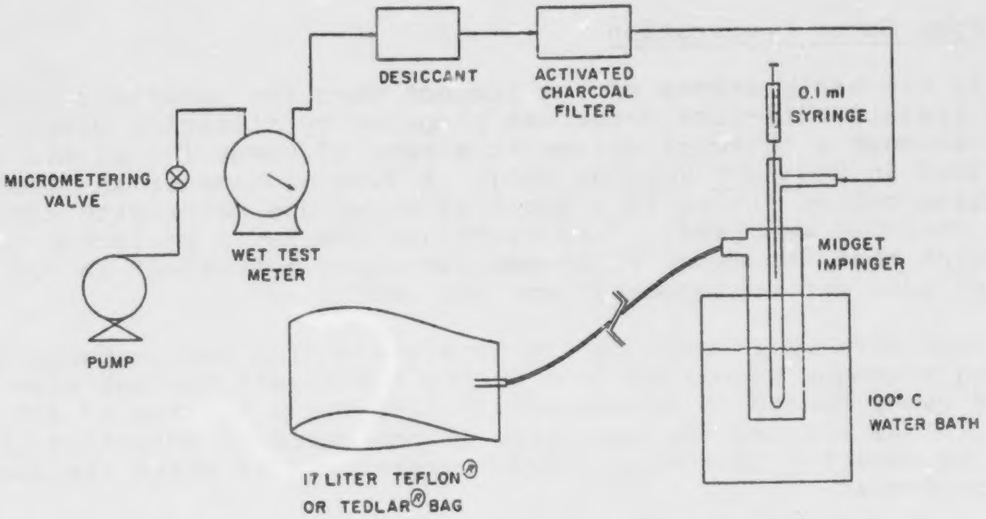
DESICCANT
ACTIVATED CHARCOAL FILTER
0.1 ml SYRINGE
MICROMETERING VALVE
WET TEST METER
MIDGET IMPINGER
PUMP
100° C WATER BATH
17 LITER TEFLON®
OR TEDLAR® BAG

Figure 1. Total odor volatilization technique.

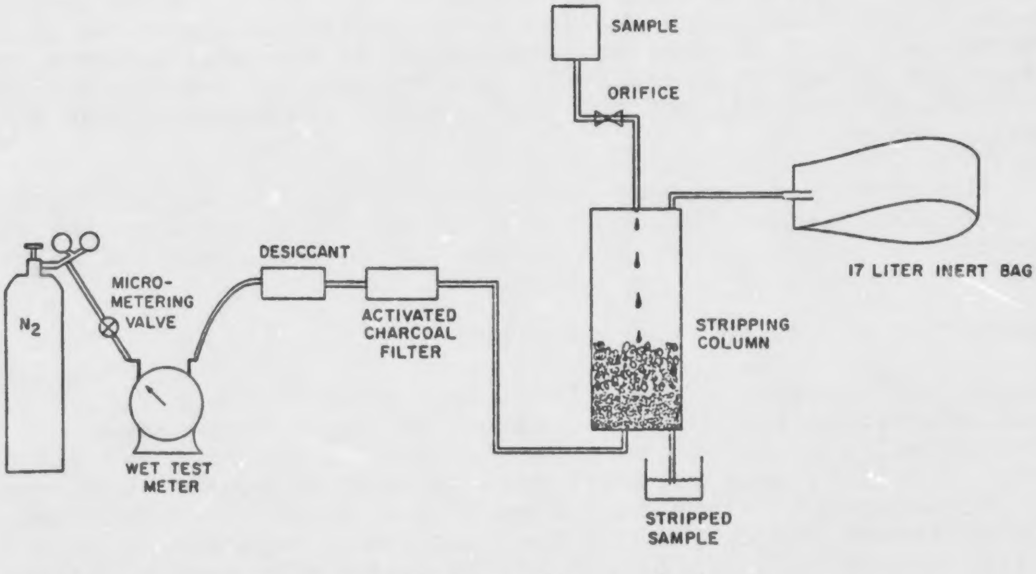
SAMPLE
ORIFICE
17 LITER INERT BAG
DESICCANT
MICRO-METERING VALVE
N2
ACTIVATED CHARCOAL FILTER
STRIPPING COLUMN
WET TEST METER
STRIPPED SAMPLE

Figure 2. Strippable odor technique.

SAMPLE PREPARATION FOR THE HEAD SPACE ANALYSIS TECHNIQUE

Odor Free Water Preparation

In the early stages of the project when the panelists were being trained, dilution water was prepared by filtering distilled water through a charcoal column at a rate of about 100 ml/min as described in Standard Methods (60). A five centimeter in diameter glass column filled to a depth of about one meter with activated charcoal was used. This technique was never perfected to the point that the water no longer exhibited a "burned" and/or "musty" odor and consequently was not used.

Odor free water used during this evaluation was prepared by purging nitrogen regulated from 200 to 500 ml/min through distilled water heated to approximately 50°C for a minimum of six hours. This allowed for stripping of the residual materials that might be detected at the elevated temperatures at which the tests were conducted.

Dilution

The samples were sequentially diluted in stages of not more than a factor of 2,000 to 1 and no less than 2.5 to 1 by use of volumetric pipettes and flasks. A stock solution of a given dilution factor was prepared. To select the dilution submitted to the panelists, the odor detectability was checked by placing 200 ml of the solution in a 500 ml large-mouth erlenmeyer flask. The flask was then placed in a 40°C water bath and allowed to equilibrate. After a sufficient period of time (five to ten minutes) the flasks were smelled to determine if there was an odor present. If no odor was present or if the odor present was judged too strong to identify an odor threshold, the appropriate corrections were made and the new solution was evaluated in a similar manner.

The procedure employed during this study had six dilutions or concentration levels with the stock solution representing the strongest dilution and each subsequent dilution stage was weaker than the previous stage by a factor of three.

PREPARATION OF THE CALIBRATION GASES

Teflon^R or Tedlar^R nine liter bags that had been filled with known quantities and dilutions of one or more of the gases, hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide were prepared from permeation tubes. Each day the chromatograph calibration curves were prepared at four or more different concentrations for each gas. Bags filled in a similar manner with one of the sulfur gases were used to screen the panelists on a regular basis.

ODOR THRESHOLD DETERMINATION BY DYNAMIC OLFACTOMETER

Principle

The dynamic olfactometer was designed for use with the forced-choice triangle test and utilized six dilution stages. The sample was diluted with charcoal filtered, odor-free room air. The unit, as shown in Figure 3, was designed by Dravnieks of the Illinois Institute of Technology (27). The samples were presented in the order of the most dilute through least dilute. The panelists were forced to identify which port in a cluster of three contained odors.

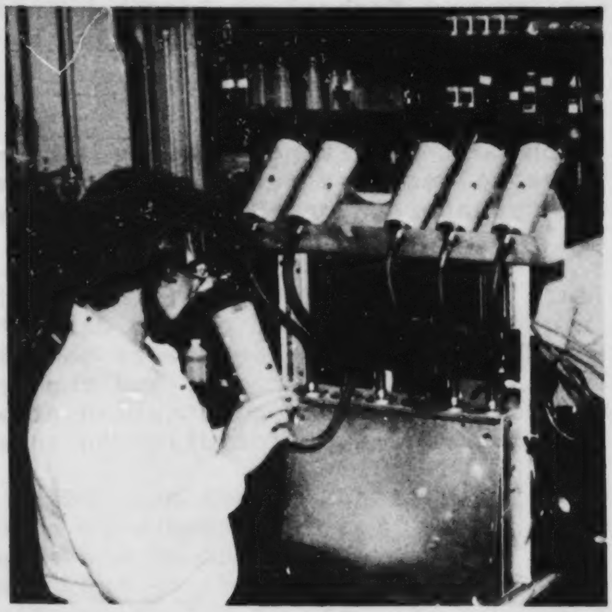

Figure 3. Forced-choice triangle dynamic olfactometer.

Data accumulated during this portion of the project included only the odor threshold or that concentration level at which a difference could be determined between the blank and sample odor.

Equipment Description

The olfactometer was used to determine the odor threshold of various process streams and to screen the panelists on a regular basis. The olfactometer received a gas sample from an inert bag at a rate of about 100 ml/min. Dilution air flow rate was about nine l/min.

Each dilution stage of the olfactometer had three ports and there were a total of six dilution stations. There were 18 individual ports for a panelist to smell in each test run. One of the ports at each dilution station received a known rate of sample from the sample bag plus a dilution air flow of approximately 500 ml/min. The other two ports received only dilution air at a rate of about 500 ml/min. The flow of sample from the bag to individual ports varied from about 3.2 to 32 ml/min.

The olfactometer flows were controlled by the use of sections of capillary tubing, with the lowest flows having the longest section of tubing. For a more complete descripition of the olfactometer, it is suggested that Source Emission Odor Measurement Via Dynamic Forced-Choice Triangle Olfactometer by Dravnieks of the Illinois Institute of Technology Research Institute and Prokop of the National Renderers Association (30) be studied.

Procedures

The flows to each port receiving a sample were measured and recorded daily. These values were recorded in the table shown in Figure 4. Flow at attenuators A and B, theoretically 27:1 were also measured daily.

Experimental data gathered while utilizing the forced-choice triangle test technique were collected on the data sheets shown in Figure 5. Included on the data sheets were sample identification, date of analysis, panelist response, and the information needed to determine the ED_{50}, that concentration at which 50 percent of the panelists detected a differentiation in odor.

Each panelist was identified by name and order of participation in the specific test. The responses were noted in the appropriate box. Only the left-hand side of the sheet was used for data collection. The right-hand side of the sheet was the table of "plotting values" utilized in the calculations described later.

Calculations

Dilution factors at each stage of the olfactometer were calculated. The flows of the sample gas (Q_s) and dilution air (Q_d) were both measured and recorded as shown in Figure 4. The dilution ratio (R_d) was calculated by the formula:

$$R_d = (Q_s + Q_d)/Q_s$$

the dilution ratio R_d was then multiplied by another constant if it was applicable, such as when a portion of the sample went through a conditioning step.

IITRI January 1974

FLOW CALIBRATIONS FOR DYNAMIC TRIANGLE
OLFACTOMETER. DATE ________________
(ALL FLOWS IN ML/MIN)

PRE-ATTENUATOR (IF ANY)		PRE-ATTENUATION Factor A	
THROUGH C	BYPASS		
5.0209	94.7297		19.8671

IF NO PRE-ATTENUATION, A=1

DILUTION LEVELS:

No.	Odor	Dilution Air	Dilution Factor D	D x A	Port No.	Log Total Dilution Factor
6	29.1971	366.9725	13.5688	269.5724	6	2.4307
5	11.0092	489.7959	45.4897	903.7471	5	2.9560
4	3.4582	444.4444	129.5190	2573.1637	4	3.4105

ATTENUATOR		Attenuation Factor B	A x B
THROUGH C	BYPASS		
8.3916	80.6939	10.6160	210.9095

DILUTION LEVELS:

No.	Odor	Dilution Air	Dilution Factor D	D x A x B	Port No.	Log Total Dilution Factor
3	31.0078	500.0000	17.1250	3611.8203	3	3.5577
2	9.8361	485.8300	50.3925	10628.2674	2	4.0265
1	3.6474	472.4409	130.5281	27529.6257	1	4.4398

Figure 4. Olfactometer flow data sheet.

ED$_{50}$ Evaluation Form for Forced-Triangle Head Space Analysis

Sample: - - - Stock Dilution = 1x10^5:1

Evaluation Date: - - - - - - RESULT: Log ED$_{50}$=5.5736 ED$_{50}$=31746x10^5 r^2=0.9598

Panelist	Name	A 1	B 2	C 3	A 4	B 5	C 6	"7"
1	A	A	A	B	B	C	Ⓒ	
2	B	A	B	B	C	C	Ⓒ	
3	C	B	B	C	C	A	B	○
4	D	A	C	B	B	Ⓑ	C	
5	E	C	C	B	Ⓐ	B	C	
6	F	B	B	A	A	A	Ⓒ	
7	G	C	A	A	B	C	Ⓒ	
8	H	B	A	Ⓒ	A	B	C	
9								
10								
	Frequency Tally			1	1	1	4	1
	Average Rank			1	2	3	5.5	8

X = Plotting Value			-1.22	-0.77	-0.43	+0.28	+1.22
Y = Log (tolerance level)	7.62	7.15	6.67	6.19	5.72	5.24	4.76

Log (dilution factor)		7.39	6.91	6.43	5.95	5.48	5.00	
Dilution no.	<1	1	2	3	4	5	6	"7"

For Rank Count

1
2
3
4
5
6
7
8
9
10

Probability Related Plotting Values

Average Rank	6	7	8	9	10
			Number of Panelists		
1.0	-1.07	-1.15	-1.22	-1.28	-1.33
1.5	-0.79	-0.89	-0.97	-1.04	-1.10
2.0	-0.57	-0.67	-0.77	-0.84	-0.91
2.5	-0.37	-0.49	-0.59	-0.67	-0.75
3.0	-0.18	-0.32	-0.43	-0.52	-0.60
3.5	0	-0.16	-0.28	-0.39	-0.47
4.0	+0.18	0	-0.14	-0.25	-0.35
4.5	+0.37	+0.16	0	-0.13	-0.23
5.0	+0.57	+0.32	+0.14	0	-0.11
5.5	+0.79	+0.49	+0.28	+0.13	0
6.0	+1.07	+0.67	+0.43	+0.25	+0.11
6.5		+0.89	+0.59	+0.39	+0.23
7.0		+1.15	+0.77	+0.52	+0.35
7.5			+0.97	+0.67	+0.47
8.0			+1.22	+0.84	+0.60
8.5				+1.04	+0.75
9.0				+1.28	+0.91
9.5					+1.10
10.0					+1.33

Figure 5. Data collection and calculation sheet for forced-choice triangle test.

The 50 percent effective dose (ED_{50}) levels were calculated in the following manner. The log of the dilution factors for each dilution stage were entered. It was assumed that when the individual was able to differentiate an odor at a particular dilution level and respond accordingly, that their true odor threshold was at some dilution between that level and the preceding more dilute level. The panelist was given "credit" for this inequity by computing the log average for these two concentration stages, and indicating that the odor was detected at this calculated level. These values are shown as "Y = log (tolerance level)" in Figure 5. The log (tolerance level) values for either extreme were obtained by assuming they were as far from the nearest log (dilution factor) value as the previous log tolerance level.

The "X = plotting value" numbers were obtained by tabulating the results of the testing. First, the "correct" answers were identified and circled as shown in Figure 5. This "correct" response correlated to the most dilute sample at which the panelists were able to detect odor and continue with correct responses after that point. The number of circles per dilution stage were then tabulated with the totals entered as shown in the "Frequency Tally" row. The "Average Rank" was then computed utilizing the column entitled "For Rank Count." Starting with the highest dilution on the left side of the page, the numbers in the "For Rank Count" column were marked with the quantity between marks the same as the numbers in the "Frequency Tally" row. Thus, as in example 1,1,1,4 and 1, numbers were checked off sequentially as they appeared in the "Frequency Tally" row. Once this had been done, the values between the marks were averaged and noted in the column entitled "Average Rank" such that in the preceding example the values were 1,2,3,5.5 and 8.

The "Average Rank" values were converted to the probability related "Plotting Values" using the table shown on the right side of the data sheet. These values are equal to probits-5 (61). The values obtained were from the column for eight panelists as circled. The Y values, log (tolerance level), were then plotted against the X values, plotting value, the ED_{50} level was the point where the log tolerance level crossed the plotting value equal to zero as shown in Figure 6. This process was simplified using the method of least squares and the formulas to determine the equation of the "best fit" line through the points as follows:

the general formula for the straight line,

Y = mx+b where m is determined by the formula

$$m = \frac{n\ xy - x\ y}{n\ x^2 - (\ x)^2}$$

and b is determined by the formula

$$b = \frac{x^2\ y - \ x\ xy}{n\ x^2 - (\ x)^2}$$

where n is the number of paired data points and

x and y are the individual data points

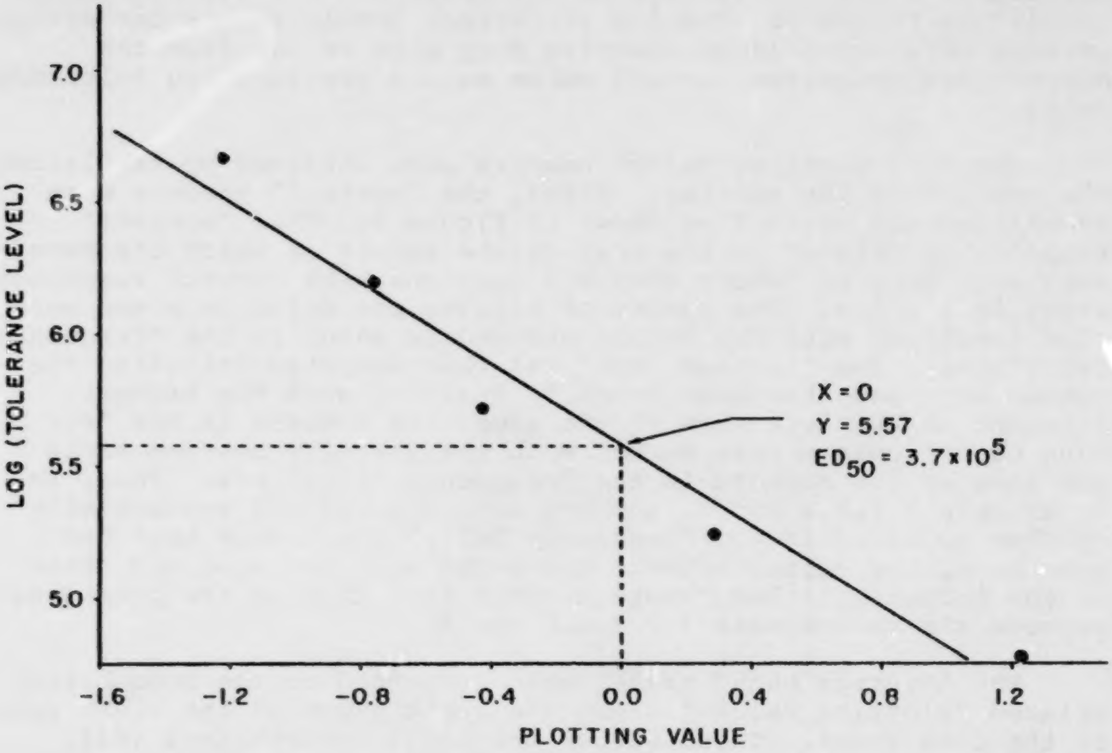

Figure 6. Plotting value vs. log (tolerance level).

The ED_{50} value was determined by substituting 0 for x in the general line equation and solving for y which was the log of the ED_{50} level. The correlation coefficient r^2 was also determined for each trial and was calculated by determining the standard deviation of the x values (S_x) and y values (S_y) by the following formulas:

$$S_x = \frac{x^2 - \frac{(\ x)^2}{n}}{n - 1}$$

$$S_y = \frac{y^2 - \frac{(\ y)^2}{n}}{n - 1}$$

and then

$$r^2 = \frac{n\ xy - \ x\ y}{n(n-1)\ S_x S_y}^{\ 2}$$

The correlation coefficient was determined for each individual run.

An example of the calculations, using the information as shown in the Figure 5 would be as follows:

$$m = \frac{5\ (-8.0878) - (-0.9200)\ (28.5784)}{5\ (3.8330) - (-0.9200)^2} = -0.7723$$

$$b = \frac{(3.8330)(28.5784) - (-0.9200)(-8.0878)}{5\ (3.8330) - (-0.9200)^2} = 5.5736$$

and substituting back into the equation for a line ($y = mx+b$) and setting $x=0$ yields $y=(-0.7723)(0)+(5.5736)=5.5736$ which is the antilog of the ED$_{50}$ which can then be calculated to be equal to 3.746×10^5. Next, the correlation coefficient is calculated by first determining the standard deviation of the x and y values as follows:

$$S_x = \sqrt{\frac{(3.8330) - \frac{(-0.9200)^2}{5}}{5 - 1}} = 0.9570$$

$$S_y = \sqrt{\frac{(165.6214) - \frac{(28.5784)^2}{5}}{5 - 1}} = 0.7544$$

and then it follows that

$$r^2 = \frac{5\ (-8.0878) - (-0.9200)(28.5784)}{(5)\ (5-1)(0.9570)(0.7544)}^{\ 2} = 0.9598$$

Another calculation used extensively in this report was the log average which was computed by adding the log of all the dilution factors of concern, determining the average of these log values, and then obtaining the antilog of that average, hence the log average.

ODOR THRESHOLD DETERMINATION BY HEAD SPACE ANALYSIS

Principle

In the head space analysis, an equilibrium is established at a preset temperature in a confined and known volume between compounds in a known liquid volume and the air space above it. The presence or absence of an identifiable odor in the head space was determined by trained panelists in this study.

Equipment Description

The head space analysis was conducted using 500 ml erlenmeyer flasks with standard taper pennyhead stoppers containing 200 ml of solution and maintained at a temperature of 40°C. Six dilution stages were used with the triangle test employed at each stage.

Procedure

The samples were presented to the panelists in the order of most dilute through least dilute. The panelists were forced to identify which flask in a series of three contained an odor and at which dilution stage the odor could be identified with a sample of the same solution that he had been exposed to earlier. This is in contrast to the olfactometer exposure method in which difference in perceived odor was a determining criteria. Before smelling each sample, the panelists were instructed to shake the stoppered erlenmeyer flask. It was hypothesized that this action established an equilibrium between the liquid and gas phases present in the closed system.

Experimental data gathered while utilizing the forced-choice triangle test technique was collected on the data sheets shown in Figure 5 in the same manner described earlier while using the olfactometer.

Calculations

The calculations for the head space analysis technique were the same as for the dynamic olfactometer with one exception. The calculation steps for determining the dilution factors at each stage of the olfactometer were not required since this step was simply recording the sample concentration in the flasks at the six dilution stages. The assumptions made earlier concerning the inequities in the computation of the log average odor threshold values also apply to this method when determining "identifiable" odor thresholds.

Alternate Head Space Procedure Used

Another method of head space analysis was used early in the process and for a limited time only. This method utilized seven flasks containing different dilutions of the process stream of interest arranged in ascending concentrations at 40°C. Interspersed with these flasks were three flasks that contained only the odor free dilution water. The panelists were asked to indicate the concentration level where they first perceived an odor that was different from a blank.

CHEMICAL ANALYSIS BY GAS CHROMATOGRAPHY

Principle

The gas chromatographic analytical procedure separates the individual constituents of a gas stream by the use of a column that selectively adsorbs and desorbs the compounds of interest at varying rates. The system utilized in this study was equipped with a flame photometric detector (FPD) which is sulfur specific at a wave length of 394 m .

Equipment Description

The chromatographic system is depicted in Figure 7. As can be seen from the figure, a hydrogen sulfide permeation tube was placed in the carrier gas stream, following the eight-port sampling valve but prior to the chromatograph oven. The tube delivered hydrogen sulfide to the detector at about 0.2 ppm. The column which contained a 3.35 x 6 mm (11 ft. x ¼ in.) Teflon^R column packed with 12% polyphenyl ether + 0.5% H_3PO_4 on a 40/60 mesh Chromasorb T column. This technique allowed a constant flow of sulfide to continuously fill the active sites on the column. In addition, it raised the background level of sulfide to the detector, since the FPD response curve indicates linear response from 5 ppb to 0.9 ppm at the detector. An electrical heating tape was used on the exhaust of the flame photometric detector to prevent condensation and subsequent intermittent blockage of the gas exit that resulted in "spikes" on the recorder readout.

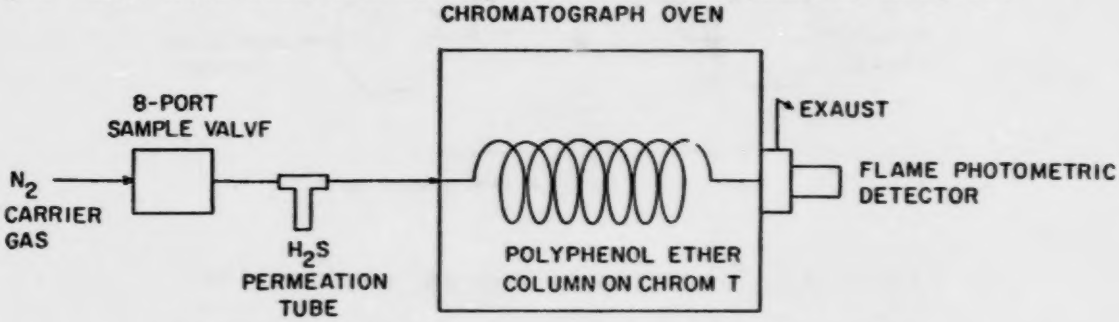

Figure 7. Chromatographic system schematic.

Procedure

The sample was purged through the eight-port sample valve and through one of the two 10 ml sample loops before injection as shown in Figure 7. The injection proper was simply the reversal of these two sample loops, trapping 10 ml of sample and injecting it to the system.

The chromatograph column oven was temperature programmed starting at 60°C for 4 minutes and increasing at the rate of 16°C per minute to 150°C which was held as long as required to elute all the peaks, generally not more than 20 minutes. The carrier gas or nitrogen flow rate was maintained at 90 ml/min and the oxygen was set at 31 ml/min. The detector and injector ovens were maintained at 105°C and the FPD block temperature was controlled at 95 to 100°C.

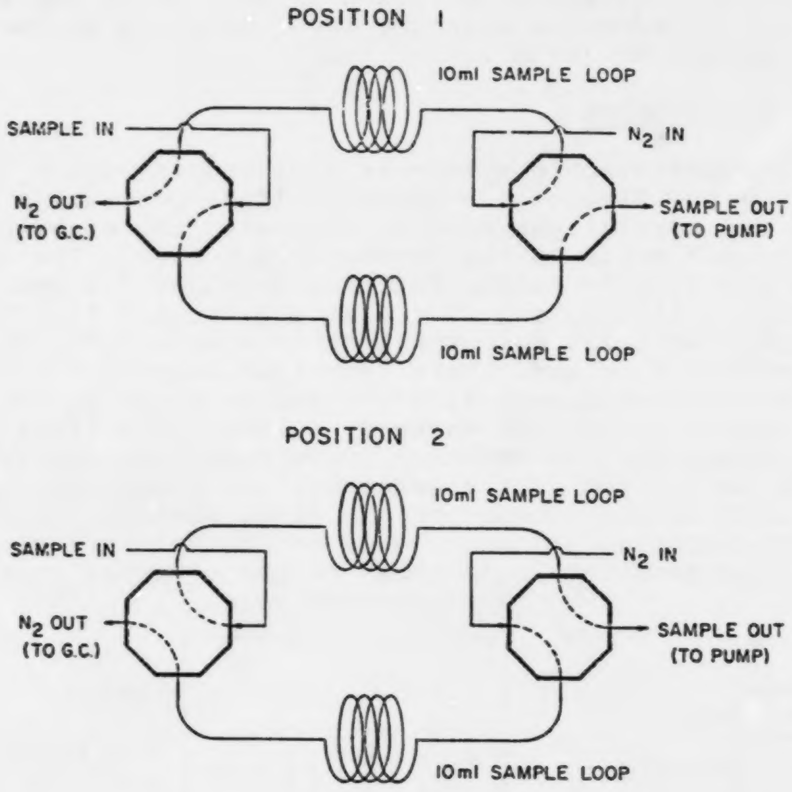
POSITION 1
10ml SAMPLE LOOP
SAMPLE IN
N2 IN
N2 OUT (TO G.C.)
SAMPLE OUT (TO PUMP)
10ml SAMPLE LOOP
POSITION 2
10ml SAMPLE LOOP
SAMPLE IN
N2 IN
N2 OUT (TO G.C.)
SAMPLE OUT (TO PUMP)
10ml SAMPLE LOOP

Figure 8. Operation of 8-port sample valve.

Calculations

Concentration of a specific gas in one of the nine liter bags was calculated by the following formula:

conc. (ppm) =

$$\frac{\left[\begin{array}{c}\text{perm rate}\\ \text{(g/min)}\end{array}\right]\left(\begin{array}{c}\text{min perm}\\ \text{tube in line}\end{array}\right)\left(\frac{22414\text{ ml}}{\text{mole}}\right)\left[\frac{\text{room temp }(^\circ\text{K})}{273^\circ\text{K}}\right]\left(\frac{1\text{ mole}}{\text{mol wt gas}}\right)}{[\text{total volume in filled bag (ml)}]} \times (10^6)$$

The daily calibration curves for the chromatographic peaks were established by comparison of peak heights for H_2S and CH_3SH and by comparison of peak areas for CH_3SCH_3 and CH_3SSCH_3.

SECTION 6

DISCUSSION OF RESULTS

ODOR THRESHOLDS OF INDIVIDUAL REDUCED SULFUR GASES BY OLFACTOMETER

By utilizing the olfactometer, permeation tubes, and Teflon^R or Tedlar^R bags, it was possible to generate standard concentrations of the reduced sulfur gases, hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide and to determining their respective odor thresholds. Bags containing one or more of these gases served as a panelist source gas on a regular basis. Odor thresholds for the reduced sulfur gases were developed and are shown in Table 4. The log average of the values obtained indicated that the gas's odor thresholds were 0.43 ppb for methyl mercaptan, 0.80 ppb for dimethyl disulfide, 1.9 ppb for hydrogen sulfide, and 3.3. ppb for dimethyl sulfide. Literature values for H_2S vary from 0.47 to 60 ppb, from 0.80 to 2.1 ppb for CH_3SH, from 0.992 to 2.6 ppb for CH_3SCH_3 and one value reported for CH_3SSCH_3 was 5.6 ppb. Thus, a good correlation for all gases with the exception of dimethyl disulfide, for which there is limited literature information available was obtained. The column entitled "max." denotes the highest odor threshold level obtained for that specific gas while "min." denotes the lowest value obtained for that specific gas.

TABLE 4. ODOR THRESHOLDS FOR REDUCED SULFUR GASES DETERMINED WITH OLFACTOMETER

Gas	No. of trials	(max) ppb	Odor threshold (log ave. ppb)	(min) ppb
Hydrogen sulfide	16	4.68	1.89	0.79
Methyl mercaptan	13	0.79	0.43	0.12
Dimethyl sulfide	13	9.82	3.31	0.55
Dimethyl disulfide	16	3.37	0.80	0.18

ODOR THRESHOLDS OF COMBINED REDUCED SULFUR GASES BY OLFACTOMETER

Cheremisinoff and Young (1) indicated that odors such as sulfides are additive. If this assumption is true, then the following equation should be true:

$$OT = \frac{[H_2S]}{OT_{H_2S}} + \frac{[CH_3SH]}{OT_{CH_3SH}} + \frac{[CH_3SCH_3]}{OT_{CH_3SCH_3}} + \frac{[CH_3SSCH_3]}{OT_{CH_3SSCH_3}} = 1$$

In the equation $[H_2S]$, $[CH_3SH]$, $[CH_3SCH_3]$, and $[CH_3SSCH_3]$, represent the concentration of that specific gas at the ED_{50} level calculated and OT_{H_2S}, OT_{CH_3SH}, $OT_{CH_3SCH_3}$, and $OT_{CH_3SSCH_3}$ represent the previously listed odor thresholds for that specific gas.

Data generated early in this study as shown in Table 5, indicated that the odor threshold of sulfide gases are not additive when measured using this technique. When considering that the odor threshold range for a specific gas could vary as much as an order of magnitude from day to day, it was not expected that the odor threshold of a complex mixture could be predicted by calculation with any degree of accuracy.

TABLE 5. ADDITIVE NATURE OF PURE SULFIDE GASES ON OLFACTORY RESPONSE

Gas combination	Log average OT (ppb)
$H_2S + CH_3SH$	0.806
$H_2S + CH_3SCH_3$	0.398
$H_2S + CH_3SSCH_3$	0.491
$CH_3SH + CH_3SCH_3$	0.192
$CH_3SH + CH_3SSCH_3$	0.291
$CH_3SCH_3 + CH_3SSCH_3$	0.232

ODOR THRESHOLD OF SELECTED STREAMS BY THE TOTAL ODOR VOLATILIZATION TECHNIQUE

A portion of this study was spent attempting to develop a technique by which the dynamic olfactometer described by Dravnieks and Prokop (28) could be utilized. In order to obtain a sample that could be delivered to the olfactometer, a total volatilization technique was developed. In this procedure, a small amount of liquid process stream effluent was volatilized in an appropriate amount of dry, odor-free air to maintain the relative humidity in the mixture below the dewpoint and was captured in either a Teflon^R or Tedlar^R bag. The technique used is presented in the section on Experimental Methods. The detectable odor threshold of the sample in the bag was then determined by the use of dynamic olfactometer and human odor panels. This method was labeled the "total odor" technique since the whole sample and therefore all compounds had been volatilized.

The data as shown in Table 6, utilized a unit, the "log average $\frac{\text{odor threshold}}{\text{ml sample}}$ /(l air)". This value was calculated by dividing the odor threshold developed using the olfactometer by the volume of liquid sample volatilized and the volume of odor-free dilution air used.

TABLE 6. TOTAL ODOR TECHNIQUE: ODOR UNIT RANGE

Source	No. of mills	No. of samples	Range ($\times 10^{-5}$) Log ave. $\frac{\text{Odor units}}{\text{ml sample}}$(l air)
Steam stripper product	2	3	14 - 350
Digester condensate	1	6	1.7 - 20
Turpentine decanter bottoms	3	7	1.2 - 27
Air stripped condensate	2	8	0.91 - 4.3
Stripper feed	6	26	0.64 - 47
MEE body condensate	2	15	0.64 - 15
MEE surface condenser	2	5	0.64 - 12
ASB influent	4	16	0.37 - 11
ASB effluent	2	9	0.25 - 6.6
Steam stripped cond.	4	10	0.15 - 14

From the data in Table 6, it can be seen that all of the process streams investigated gave the same range of values. This included such widely variant steams as the treated liquid from a steam stripper, turpentine decanter underflows and aerated stabilization basin effluents, etc. Observation based on odor intensity of the head spaces above stored samples by the investigators indicated this to not be the case. It was hypothesized that the volatilization of the entire sample allowed compounds that would not normally volatilize with the degree of turbulence encountered in sewers and waste treatment systems to do so. Following this line of reasoning, compounds not normally volatilized were assumed to be contributing significantly to the detectable odor threshold which was measured using this procedure. Alternate procedures, judged to more closely simulate the turbulence encountered within a mill environment, for generating the odor panels source gas were then investigated.

ODOR THRESHOLD OF SELECTED STREAMS BY THE OLFACTOMETER AND STRIPPING TECHNIQUE

Since there did not appear to be a significant difference in the odor threshold levels developed by the "total odor" technique, a stripping technique was used in an attempt to more closely simulate the odor liberation process from the treatment facility and sewer lines. This method included the use of an olfactometer for determinable odor threshold as previously discussed. Samples were prepared by nitrogen stripping and capturing the off-gases. The technique used is presented under the appropriate section of the Experimental Methods section of this report.

On a trial run, this method yielded odor threshold values that were similar to the "total odor" technique results. Variation was only about 100 fold between the cleaner samples observed to have a low odor level, such as the aerated stabilization basin effluent, and the samples with high odor intensity such as digester condensates. These results are shown in Table 7. It was interesting to note that in general, these values were 2 to 3 orders of magnitude smaller than those derived by the "total odor" technique indicating that, turbulence or a gas-liquid interface phenomena plays a significant role in the amount of evolved and measured detectable odor of an effluent or process stream. Alternate means for simulating the turbulence encountered by effluent streams at mill sites were considered. Being largely emperical, they were not pursued and more conventional methods for odor generating from a liquid and its measurement were pursued.

TABLE 7. STRIPPING TECHNIQUE: ODOR UNIT RANGE

Source	Log ave.	Range ($x10^{-5}$) Odor units / ml sample	(liter air)
Digester condensate		0.043 -	0.23
Lab aerated digester condensate		0.0032 -	0.0074
Clarifier outlet		0.0015 -	0.0057
ASB effluent		0.0015 -	0.0031

RELATIONSHIP OF MEASURED REDUCED SULFUR CONCENTRATIONS TO THE ODOR THRESHOLDS

During the portion of this investigation in which the odor threshold values were determined with the panelists using the olfactometer, the concentration of reduced sulfur gases in the bag introduced to the olfactometer were determined with the gas chromatograph equipped with a flame photometric detector.

The measured concentration of reduced sulfur compounds were compared with the odor threshold determined for each sample analyzed. For each source with more than three samples, the correlation coefficient (r^2) between the concentration of the reduced sulfur compounds and the odor threshold varied from 0.00046 to 0.171. Similarly, the correlation coefficient (r^2)

varied from 0.011 to 0.190 when comparing the odor threshold determined for the sample bag to that calculated from the reduced sulfur gas analysis. These calculated values for the correlation coefficient were deemed low and indicated no correlation between the measured reduced sulfur concentration in the sample and its odor thresholds.

It was further determined that the individual reduced sulfur gases were not additive in their contribution to the perceived odor threshold when using this methodology.

PRELIMINARY ODOR THRESHOLD MEASUREMENT BY THE HEAD SPACE ANALYSIS TECHNIQUE

With the lack of variation in odor threshold measured when employing either the "total odor" or "stripping" techniques for sample generation and using the olfactometer, use of the head space method of odor analysis was investigated. The procedure used in this preliminary study utilized seven flasks of different concentrations of the stream of concern arranged in ascending order with flasks containing odor-free water interspersed among them. The panelists were asked to identify the first flask in which they could detect an odor.

The results, as shown in Table 8, indicated that detectable odor thresholds determined by this technique varied over a range of five orders of magnitude. These values were more in order with the investigators observed odor intensity of the head space of these streams in containers. For this reason a head space analysis procedure was selected for use in this study.

TABLE 8. PRELIMINARY HEAD SPACE TECHNIQUE: ODOR UNIT RANGE BY SOURCE

		Range ($\times 10^{-5}$)	
Source	Log ave.	$\frac{\text{Odor units}}{\text{ml sample}}$	liter air
Digester condensates		0.0045	- 0.049
Lab aerated digester condensate		0.000028	- 0.00056
Clarifier outlet		0.00000036	- 0.00000081
ASB effluent		0.00000039	- 0.0000019

THE EFFECTS OF INITIAL STOCK SOLUTION CONCENTRATION AND ODOR STABILITY ON THE DETECTABLE ODOR LEVEL IN THE HEAD SPACE ANALYSIS

As the early trial period progressed, it became obvious to the investigators that the response of the panelists may have been dependent upon the original sample stock solution concentration. Therefore, different detectable odor thresholds could be

TABLE 9. EFFECT OF STOCK SOLUTION DILUTION LEVEL ON ODOR THRESHOLD VALUES AS DETERMINED FOR MEE SURFACE CONDENSER CONDENSATE FROM MILL C BY PANELS OF SIX

Run	Number of panelists per flask	Stock dilution	Dilutions of odor threshold $(x10^{-5})$	Number of panelists missed	
				high	low
1	2x2x2	3.2 x 10^{10}:1	5,300,000	2	2
2	3x3	3.2 x 19^{10}:1	3,300,000	0	0
3	x6	3.2 x 10^{10}:1	1,400,000	0	1
4	x6	3.2 x 10^{10}:1	4,000,000	1	0
5	x6	3.2 x 10^{10}:1	1,400,000	1	2
6	2x2x2	2.56x 10^{17}:1	13,000,000,000,000	0	1
7	3x3	2.56x 10^{17}:1	5,300,000,000,000	2	0
8	x6	2.56x 10^{17}:1	230,000,000,000,000	1	0

measured for the same source. Leonardos, *et al.*, (24) called attention to this phenomena in their work.

To learn if the above effect was biasing the results, the initial stock solution concentration for the preparation of a series of samples was changed. A trial was run utilizing multiple-effect evaporator surface condenser condensates. The panelists were given a sample prepared from stock solution dilutions of $3.2\text{x}10^{10}$:1 and $2.56\text{x}10^{17}$:1. The head space analysis was set up for the forced triangle test, that is one flask in three at each concentration level to which the panelists were subjected contained the samples. This allowed a factor of 243 difference between the most concentrated and weakest dilution in the series. The results shown in Table 9 indicated that there was a difference recognizable to the panelists between the blank flasks and the flasks containing sample since the dilution level at which a response to odor was detected could be calculated for both dilution series. The calculated ED_{50} appeared to vary in proportion with the dilution factor of the stock solution.

The results indicated that two stock solutions, one at $3.2\text{x}10^{10}$:1 and the other at $2.56\text{x}10^{17}$:1 which were made from the same sample and given to the panelists for evaluation yielded distinctively different but seemingly valid odor thresholds. This indicated that the calculation of an odor detection level by determining which flask smelled "different" was not a valid testing procedure for the purposes of this study.

Odor Stability

Table 9 presents one additional piece of information, the column entitled "Number of Panelists per Flask." This is the number of panelists that smelled a single sample from identically prepared flasks and the number of sample flasks used at each concentration level during that run. For example 2x2x2 indicates that six panelists participated in that run, two panelists each per sample flask were used prior to exchanging that flask for an identically prepared sample, and a total of three flasks were used at each dilution level. Additionally, 3x3 means 6 panelists were used, two identically prepared sample flasks were utilized, being exchanged when three panelists had used them. Finally, x6 signifies that six panelists were used and all six made their odor determinations using the same flask containing the sample at each concentration level. These data indicated that there was no significant variation in the detectable odor threshold for the effluent used in this study by six or less panelists using the same set of flasks. However, the head space analysis method for determing odor thresholds is prone to the loss of volatile compounds which could be responsible for the odor and the above is not intended to be applied as a general rule.

REASONS FOR CHOOSING IDENTIFIABLE ODOR LEVEL OVER DETECTABLE ODOR LEVEL IN THE HEAD SPACE ANALYSIS TECHNIQUE

For the reasons previously explained and shown in Table 9, namely the original sample stock solution concentration could bias the determined odor threshold level, alternate approaches were considered. That selected was the identifiable odor threshold. In this procedure the panelists were required to smell the odor of the diluted sample prior to smelling the test flasks and were instructed to respond to the odor in the flask that first smelled similar to the sample odor.

The head space analysis data was generated after refinement of the techniques for this procedure and conditioning the panelists to the test and mode of operation. Since there was a factor of three difference in the sample concentration between dilution stages, any results within a factor of three were considered as virtually the same value.

NUMBER OF DILUTION STAGES EFFECT ON THE IDENTIFIABLE ODOR THRESHOLD

Since this project addressed odor, or volatile constituents of the mill process streams and often required dilutions of several orders of magnitude prior to testing, there was concern for the ability to maintain the integrity of the sample during dilution. The same sample, subjected to different dilution sequences might actually yield a different value for the ED_{50} due to systematic errors.

To determine what effects, if any, might be caused by the number of dilution stages to which the sample was subjected, an investigation was undertaken.

Data presented in Table 10 shows that the number of dilution stages used in preparation of the sample did not have a significant effect on the identifiable odor threshold. The only exception, was the last sample of vapor compression evaporator condensate from Mill I (runs 8a and 8b). However, the bulk of the data indicated the number of dilution stages was of little or no concern in the preparation of samples. Thus, the results indicated that there were no systematic errors associated with the number of dilution stages used in preparation of the sample. Even when diluted in three different manners, the ED_{50} values measured were similar.

A brief explanation of the table format is in order. Table 10 is similar to most presented in the remainder of this report. The column entitled "ED_{50} Dilution Factor" is the column of interest and signifies the dilution at which 50 percent of the panelists identified the characteristic odor of the sample. These values have all been multiplied by a factor of 10^{-5} prior

TABLE 10. EFFECT OF DILUTION STAGES ON IDENTIFIABLE ODOR

Run	Sample	Mill	No. of dil. stages	No. of panel.	No. of panel ident. odor at all dil.	Maximum test dil. ($\times 10^{-5}$)	ED_{50} dil. factor ($\times 10^{-5}$)	No. of panel. missed low	Min. dil. at level missed ($\times 10^{-5}$)
1a	S.C. cond.	C	2	9	0	-	21	0	-
1b			3	8	0	-	12	2	2.3
2a	S.C. cond.	C	2	8	0	-	17	1	2.3
			3	9	0	-	19	2	2.3
3a	S.C. cond.	C	2	7	0	-	19	1	2.3
3b			2	9	0	-	22	1	2.3
3c			2	9	0	-	22	1	2.3
3d			3	8	0	-	14	2	2.3
4a	Conc. cond.	I	2	8	0	-	1.8	0	-
4b			3	8	0	-	0.85	0	-
5a	Conc. cond.	I	1	8	0	-	0.12	0	-
5b			2	8	0	-	0.16	0	-
6a	Conc. S.C. cond.	I	1	8	0	-	1.2	0	-
6b			2	8	0	-	0.81	2	0.12
7a	VCE cond.	I	1	8	0	-	16	0	-
7b			2	8	0	-	12	0	-
7c			3	8	0	-	24	0	-
8a	VCE cond.	I	2	8	0	-	16	0	-
8b			3	8	0	-	2	0	-

to entry. The number of panelists that participated in the test is also indicated. On a few samples, some panelists either identified the odor at all six dilution levels or failed to identify it at all dilution levels. Criteria were established to determine the validity of a sample run as follows: (a) if more than one-half of the panelists failed to identify the odor in the range of dilutions, the run was discarded, (b) if two or more panelists in a team of six, seven, or eight, or three or more panelists in a team of nine or ten identified the odor at all the dilution stages, the ED_{50} was noted as "greater than" ( ) the calculated value using all panel participants, and (c) if two or more panelists in a team of six, seven, or eight, or three or more panelists in a team of nine or ten failed to identify the odor at all the dilution stages, the ED_{50} was noted as "less than" ( ) the calculated value using all panel participants observations.

An entry in the "Maximum Test Dilution" column signifies the lowest effluent concentration of that run at which one or more of the panelists detected the identifiable sample odor at all test dilutions.

An entry in the "Min. Dil. at Level Missed" column signifies the highest effluent concentration of that run at which one or more of the panelists failed to detect the identifiable sample odor at that concentration.

STOCK DILUTION LEVEL EFFECT ON THE IDENTIFIABLE ODOR THRESHOLD

The panelists were required to smell the odor of the diluted sample prior to smelling the test flasks and were instructed to respond to the odor in the flask that first smelled similar to the sample odor. This proved to be a more reliable value since it could be duplicated when starting with different stock dilutions as shown in Table 11. The only discrepancy noted was in run 1 and appeared to be associated with the number of panelists per bottle rather than the initial dilution of the stock solution. The discrepancy, however, was not considered significant. Runs 2 and 3 displayed essentially the same "identifiable" odor threshold when the dilutions were prepared from different stock solutions. The results also indicated that as many as 7 panelists could be run per dilution series without affecting the results.

RESULTS OF DUPLICATE SAMPLES ON IDENTIFIABLE ODOR THRESHOLDS

Throughout this study, duplicate runs were made on individual samples. Duplication, in this context, means the individually prepared dilution series of the sample was presented to the panelists two, three, and four times during the day.

The results of these duplicate runs are shown in Table 12. The last column of the table was derived by dividing the largest

TABLE 11. EFFECT OF STOCK SOLUTION DILUTION LEVEL ON IDENTIFIED ODOR THRESHOLD VALUES AS DETERMINED FOR TREATED TOTAL MILL EFFLUENT FROM MILL C

Run	No. of panel. per flask	Stock dilution	No. of panelists ident. odor at all dil.	Maximum test dilution ($x10^{-5}$)	ED_{50} dilution factor ($x10^{-5}$)	No. of panelists "missed low"	Min. dil. at level missed ($x10^{-5}$)
1	x6	100:1	0	-	0.0083	0	-
	3x3	100:1	1	0.42	0.095	0	-
	x6	25:1	0	-	0.0059	0	-
	3x3	25:1	3	0.11	0.043	0	-
2	x7	500:1	0	-	0.021	1	0.0029
	3x4	500:1	1	2.1	0.053	0	-
	x7	50:1	0	-	0.026	0	-
3	3x4	100:1	0	-	0.013	0	-
	x7	100:1	0	-	0.020	0	-
	3x4	25:1	0	-	0.022	0	-
	x7	25:1	1	0.11	0.019	0	-

ED_{50} recorded on a particular sample by the smallest ED_{50} recorded for that same sample. The largest factor between any two runs was 3.34 for run 23. The smallest difference between two runs was a factor of less than 1.1 for run 2. The average factor between duplications on 23 runs was 1.8.

Results of these tests indicated that the panels were capable of duplicating their observations on samples prepared in a similar manner.

STORAGE STABILITY OF ODOR IN SAMPLE BOTTLE

There was concern for the sample stability when shipped across the country which required several days transit time. Tests were run to determine the storage stability of samples that were analyzed several days after collection.

The results of this study are presented in Table 13. The study can be broken into two segments, the first, runs 1 through 4 and the second, runs 5 through 7. In the first four runs, the samples analyzed on the second day were from the same bottle. The second set of three runs were analyzed on duplicate samples such that the first time each bottle was opened was the day on which it was analyzed.

The first four runs gave inconclusive results. The first two samples indicated that the odor intensified in the sample bottles after exposure to air several days prior to analysis. This was opposite of the anticipated results. The potential for oxidation of sulfides and loss of volatiles through the air space above the sample would be expected to yield an identifiable odor threshold at a lower dilution. Runs 3 and 4 indicated storage stability of previously opened sample bottles was good.

These mixed results prompted additional study of sample storage stability, hence runs 5, 6, and 7. These three samples were collected in triplicate, refrigerated and tested after one or two, seven, and ten days of storage. Only two bits of data might appear irregular. The first, the turpentine decanter underflow value obtained on March 14, was somewhat high when compared to the low "identifiable" odor threshold of March 8. However, since both of these values were within a factor of three of the median threshold measured on March 17, the concern was minimal. The second was also minor and concerns the data generated from the multiple-effect (MEE) hot well sample analyzed on March 17. The value recorded is low, but was also noted as "greater than" the value presented. Both the high and the low values from this set of data were within a factor of three from the mean.

It was concluded from this exercise that samples could be stored in completely filled glass containers under refrigerated conditions for periods of up to ten days. During this study a

TABLE 12. DUPLICATE SAMPLE IDENTIFIABLE ODOR DETERMINATIONS ON THE SAME DATE

Run	Sample	Mill	Date analyzed	No. of panel.	No. of panelists ident. odor at all dil.	Maximum test dilution ($\times 10^{-5}$)	ED_{50} dilution factor ($\times 10^{-5}$)	No. of panel. missed low	Min. dil. at level missed ($\times 10^{-5}$)	Largest ED_{50} / smallest ED_{50}
1	Surface condenser condensate*	C	1/20/78	9 8	0 0	- -	21 < 12	0 2	- 2.3	1.8
2	Surface condenser condensate†	C	1/20/78	8 8	0 0	- -	17 < 19	1 2	2.3 2.3	<1.1
3	Surface condenser condensate ‡	C	1/20/78	7 8 9 9	0 0 0 0	- - - -	19 < 14 22 22	1 2 1 1	2.3 2.3 2.3 2.3	>1.6
4	Surface condenser condensate	C	1/26/78	7 7	0 0	- -	1.9 2.6	0 0	- -	1.4
5	#3 MEE body condensate	C	1/26/78	7 7	0 0	- -	0.021 0.017	0 0	- -	1.2
6	Chlorination stage filtrate	C	2/02/78	6 6	0 0	- -	< 0.00081 0.0011	0 0	- -	1.4
7	Chlorination stage condensates	C	2/02/78	6 6	0 0	- -	11 4.7	0 0	- -	2.3
8	Concentrator condensate	I	2/09/78	8 8	0 0	- -	1.8 0.85	0 0	- -	2.1
9	VCE condensate	I	2/09/78	8 8 8	0 0 0	- - -	12 24 16	0 0 0	- -	2.0
10	Conc. S.C. condensate	I	2/10/78	8 8	0 0	- -	1.2 0.81	0 2	- 0.12	>1.5
11	Concentrator condensate	I	2/10/78	8 8	0 0	- -	0.12 0.16	0 0	- -	1.3
12	VCE condensate	I	2/10/78	8 8	0 0	- -	2.0 5.3	0 0	- -	2.7
13	Stripper feed	F	2/14/78	7 7	0 0	- -	350 350	1 1	120 120	1.2

(continued)

TABLE 12. (continued)

Run	Sample	Mill	Date analyzed	No. of panel.	No. of panelists ident. odor at all dil.	Maximum test dilution ($x10^{-5}$)	ED_{50} dilution factor ($x10^{-5}$)	No. of panel. missed low	Min. dil. at level missed ($x10^{-5}$)	Largest ED_{50} smallest ED_{50}
14	#2 concentrator condensate	D	2/16/78	8	0	–	0.44	1	0.058	
				8	0	–	1.2	0	–	2.7
15	#2 MEE body condensate	D	2/16/78	8	0	–	0.87	0	–	
				8	0	–	0.69	0	–	1.3
16	#2 MEE body condensate	D	2/17/78	7	0	–	0.89	0	–	
				7	0	–	2.1	0	–	2.4
17	#4 MEE body condensate	D	2/17/78	7	0	–	0.89	0	–	
				7	0	–	1.3	0	–	1.5
18	VCE condensate	J	2/28/78	6	0	–	540	0	–	
				6	1	8400	940	0	–	1.7
19	Turpentine decanter underflow	J	2/28/78	6	0	–	63	0	–	
				6	0	–	58	0	–	1.1
20	#2 MEE body condensate	E	3/02/78	8	0	–	2.2	0	–	
				8	0	–	2.7	0	–	1.2
21	#2 MEE body condensate	B	4/07/78	7	0	–	< 13	3	5.8	
				7	0	–	< 16	3	5.8	1.2
22	Decker filtrate (black liquor)	A	4/12/78	6	2	2.1	> 0.23	0	–	
				6	2	21	> 0.76	0	–	3.3
23	Turpentine decanter underflow	E	4/12/78	6	0	–	< 36	2	20	
				6	0	–	120	1	20	> 1.3
									n =	23
									$\bar{x}$ =	1.2

* 1/3 of panelists/flask, 3 flasks/test
† 1/2 pf panelists/flask, 2 flasks/test
‡ All panelists on same flask, 1 flask/test

TABLE 13. STORAGE STABILITY STUDIES ON MILL E SAMPLES

Run	Sample	Date sampled collected	Date sampled analyzed	No. of panel.	No. of panelists ident. odor at all dil.	Maximum test dilution (x10^{-5})	ED$_{50}$ dilution factor (x10^{-5}	No. of panelists missed low	Min. dil. at level missed (x10^{-5})
1a	#2 MEE body cond.*	3/2/78	3/3/78	8	0	–	1.8	0	–
1b			3/7/78	8	2	420	<16	1	0.58
2a	# 5 MEE body cond.*	3/2/78	3/3/78	8	1	4.2	1.1	0	–
2b			3/7/78	8	3	4200	>470	0	–
3a	MEE hot well*	3/2/78	3/3/78	8	1	840	55	0	–
3b			3/7/78	8	1	840	79	0	–
4a	Turp. decanter underflow*	3/2/78	3/3/78	8	2	8400	>1200	0	–
4b			3/7/78	8	2	8400	>1100	0	–
5a	#3 MEE body cond.+	3/7/78	3/8/78	7	0	–	5.4	1	1.2
5b			3/14/78	9	0	–	0.75	1	0.12
5c			3/17/78	6	0	–	2.2	0	–
6a	Turp. decanter underflow+	3/7/78	3/8/78	7	0	–	72	1	12
6b			3/14/78	9	0	–	120	0	–
6c			3/17/78	6	0	–	88	0	–
7a	MEE hot well+	3/7/78	3/9/78	7	0	–	9.0	0	–
7b			3/14/78	9	0	–	15	0	–
7c			3/17/78	6	2	8.4	>2.4	0	–

* Samples not kept sealed prior to use on second date listed

+ Samples kept sealed prior to use on second and third date (individualized samples for each source and date) total of 181 different samples were processed and only 27 were stored for a period exceeding eighteen hours.

SUMMARY OF HEAD SPACE ANALYSIS PROCEDURE EVALUATION

The procedure evaluation indicated that the panelists should be required to express their response on the basis of the dilution stage at which an identifiable odor similar to that of the sample was recognized. The preliminary investigation showed that for these samples as many as 6 panelists could be used on a single solution series without the solution losing its odor integrity. The storage stability study indicated that samples collected in completely filled glass bottles could be stored under refrigerated conditions for periods of up to ten days.

IDENTIFIABLE ODOR THRESHOLDS OF PROCESS LIQUOR STREAMS

White Liquor

Samples of white liquor were obtained for odor analysis. This stream is the pulp cooking liquor and has an in-process flow rate of about 3100 liters/metric ton (750 gal/ton) at 15 to 20 percent solids is an in-process stream and loss to the sewer is only intermittent through spills or other process abnormalities. Two samples were obtained from different locations. The identifiable odor threshold varied from about $2.0x10^{7}$ to $4.0x10^{7}$ as shown in Table 14.

Green Liquor

Samples of green liquor were also obtained for odor threshold determination. This in-process flow results from dissolution of the inorganics in the heat recovery furnace smelt and is the first step in cooking liquor manufacturing step. It represents a flow at about 3750 liters/metric ton (900 gal/ton) at about 15 to 20 percent solids and losses are only due to spills or process irregularities. Three samples were obtained from two different mills. The identifiable odor threshold values measured from these samples varied from less than $2.6x10^{6}$ to as high as $6.3x10^{7}$ as shown in Table 14.

Weak Wash

The third in-process stream analyzed was the weak wash or that liquid stream recycled in the causticizing system. The in-process flow of this stream is about 4,200 liters/metric ton (1,000 gal/ton) at 4-9% solids. Two samples were obtained from different mills. The results as shown in Table 14, indicated that the identifiable odor threshold had a range of $9.0x10^{6}$ to $4.0x10^{7}$.

TABLE 14. IDENTIFIABLE ODOR THRESHOLD OF IN-PROCESS STREAMS

Run	Mill ident.	No. of panel.	No. of panelists ident. odor at all dil.	Maximum test dilution ($x10^{-5}$)	ED_{50} dilution factor ($x10^{-5}$)	No. of panelists "missed low"	Min. dil. at level missed ($x10^{-5}$)
White liquor							
1	C	6	0	-	200	0	-
2	E	6	0	-	410	0	-
Green liquor							
3	C	6	0	-	<26	2	5.0
4	C	8	2	8400	>170	0	-
5	E	6	0	-	630	0	-
Weak wash							
6	C	8	0	-	90	0	-
7	F	7	0	-	400	0	-
Black liquor							
8	C	7	0	-	0.31	0	-
9	C	7	0	-	0.10	0	-

TABLE 15. IDENTIFIABLE ODOR THRESHOLD OF NON-COMBUSTIBLE LINE CONDENSATE

Run	Mill ident.	No. of panel.	No. of panelists ident. odor at all dil.	Maximum test dilution ($x10^{-5}$)	ED_{50} dilution factor ($x10^{-5}$)	No. of panelists "missed low"	Min. dil. at level missed ($x10^{-5}$)
1	E	6	0	-	1,100	0	-
2	E	7	0	-	11,000	1	1200

Streams Containing Black Liquor

These were effluent streams that are associated with the pulp washing or screening process. Samples were collected from two different locations at one mill. The first sample was collected after the final stage of conventional pulp washers and the second was collected after the decker. At this location the decker was used as a last stage of pulp washing. The filtrate from the decker was used as wash water on the last conventional washer stage. The soda content in the pulp from this "decker" averaged about five kilograms per metric ton (10 lbs/ton). The black liquor flow at the last conventional stage brown stock washer was measured at about 10,000 liters/metric ton (2,300 gal/ton) at less than 1 percent solids from the "decker" filtrate.

The ED_{50} identified odor threshold values obtained were $3.1x10^4$ for the washer sample and $1.0x10^3$ for the sample from the "decker" as shown in Table 14.

Summary of Process Liquor Streams Identifiable Odor Threshold Measurements

As a category, these in-process liquor streams generally had the highest identifiable odor thresholds of any of the streams measured during this survey. Identifiable odor thresholds were measured in the range of $2.6x10^6$ to $6.3x10^7$ with the exception of the sample containing black liquor with ED_{50} values found of $1.0x10^3$ and $3.1x10^4$.

Distinctively, these process streams did not smell particularly strong prior to analysis. However, after dilution it became apparent that the odor intensities increased. All four streams are normally basic and contain high concentrations of sulfides in solution. Dilution of these process streams resulted in lowering of pH, the liberation of sulfides and an increase in the odor threshold of the process stream. This is similar to the process that would occur at the mill site upon addition of these liquors to the mill's sewer system and treatment plant.

IDENTIFIABLE ODOR THRESHOLD OF OTHER PROCESS STREAMS

Noncondensible Line Condensates

Two samples of condensate from a noncondensible gas handling system were obtained from a 544 metric ton/day (600 ton/day) kraft mill with about 200 metric ton/day (225 ton/day) NSSC pulp. The condensates were from the noncondensible line conveying kraft batch digester combined with multiple-effect evaporator noncondensibles to the lime kiln. The samples collected had identifiable odor thresholds of $1.1x10^8$ and $1.1x10^9$ as shown in Table 15. These were the highest of any single process stream measured during this survey, however, the flow was minimal.

Turpentine Decanter Underflow

Nine analyses were run on turpentine decanter underflow from six different mills including two from the southeastern United States. The log average of the identifiable odor threshold was 7.2×10^6 with a miximum of 1.2×10^8 and a minimum of 2.9×10^5 as shown in Table 16.

This source had a flow varying from 124 liters/metric ton at mill I to 650 liters/metric ton at mill H (30 gal/ton to 156 gal/ton). Mill E, which had the highest dilution factor for the identifiable odor threshold, was a West Coast mill which used relatively fresh chips. Mills A and B, southeastern mills, tended to require a high dilution before reaching the ED_{50} identifiable odor threshold.

Vapor Compression/Recompression Evaporator Streams

One of the more recent innovations in black liquor evaporation has been the use of vapor compression or recompression evaporators as a first stage of black liquor evaporation. These systems usually use excess steam from another source. The units typically have two effluent streams, the steam condensate and the vapor condensate.

The vapor condensate stream typically required a high dilution to odor threshold. The flow of this stream was about 250 liters/metric ton (60 gal/ton) of pulp production. As shown in Table 17, the identifiable odor threshold of the vapor condensate varied from 2.0×10^5 to 9.4×10^7 with a log average of 3.0×10^6.

Pulp Cleaning Effluent

Six samples containing decker filtrate were analyzed from three different mills. The results are presented in Table 18. The samples were only collected from deckers following screen rooms.

The identifiable odor thresholds varied from 7.8×10^2 to $>4.2\times10^6$. Mills A and B were bleached kraft mills and mill E was a linerboard mill. The variations in the identifiable odor thresholds noted at mill A, 7.8×10^2 for run 1 and $>7.6\times10^4$ for run 2, could be attributed to a suspected increase in black liquor carryover since the conductivity of the sample for run 2 was approximately four times that of run 1. At mill B, the variation in the identifiable odor threshold of 9.6×10^5 to 8.1×10^2, might have been partially attributed to the pine pulp on the first decker and hardwood pulp on the second decker.

Mill E was a kraft mill with some neutral sulfite pulping. The kraft pulp following the three drum, four stage brown stock

TABLE 16. IDENTIFIABLE ODOR THRESHOLD OF TURPENTINE DECANTER UNDERFLOW

Run	Mill ident.	No. of panel.	No. of panelists ident. odor at all dil.	Maximum test dilution (x10^{-5})	ED_{50} dilution factor (x10^{-5})	No. of panel "missed low"	Min. dil. at level missed (x10^{-5})	Flow 1/metric ton
1	A	6	0	-	<36	2	20	
2	A*	6	0	-	120	1	20	
3	B	6	0	-	870	0	-	0.088
4	E	8	1	84,000	1100	2	120	
5	E	8	2	8,400	>1200	0	-	0.14
6	H	6	0	-	160	0	-	0.46
7	I	8	0	-	3.5	1	1.2	
8	I	8	0	-	2.9	0	-	0.070
9	J	6	0	-	63	0	-	
10	J*	6	0	-	58	0	-	
11	J	7	0	-	7.2	1	1.2	0.27
			Log average		72			

* Duplicate run - log average of duplicates used in column log average

TABLE 17. IDENTIFIABLE ODOR THRESHOLD OF VCE CONDENSATES

Run	Mill ident.	No. of panel.	No. of panelists ident. odor at all dil.	Maximum test dilution $(x10^{-5})$	ED_{50} dilution factor $(x10^{-5})$	No. of panelists "missed low"	Min. dil. at level missed $(x10^{-5})$
1	F	7	1	840	22	0	-
2	F	6	0	-	110	0	-
3	I	8	0	-	12	0	-
4	I*	8	0	-	24	0	-
5	I*	8	0	-	16	0	-
6	I	8	0	-	2.0	0	-
7	I*	8	0	-	5.3	0	-
			Log average		7.4		
8	J	6	0	-	540	0	-
9	J*	6	1	8400	940	0	-
10	J	7	0	-	8.2	0	-
			Log average		30		

* Duplicate or triplicate run-log average used in column log average

TABLE 18. IDENTIFIABLE ODOR THRESHOLD OF DECKER FILTRATE

Run	Mill ident.	No. of panel	No. of panelists ident. odor at all dil.	Conc. of highest dilution	ED_{50} dilution factor	No. of panel. "Missed low"	Min. dil. at level "missed"	Conductivity (mhos/cm)
1	A	6	1	0.21	0.0078	0	-	670
2	A*	6	2	21	$>$0.76	0	-	2500
3	B	6	0	-	9.6	0	-	610 (pine)
4	B*	6	0	-	0.0081	0	-	325 (hardwood)
5	E	6	6	42	$>$42	0	-	$\sim$1400
6	E	7	0	-	18	1	0.58	$\sim$1400
	Decker filtrate log average				0.84			

* Second decker at same mill

washer was diluted prior to a refiner, low density storage and screening followed by a decker that was operated as a thickener.

Black Liquor Concentrator Condensates

There are several sources of condensate generation within the kraft pulping black liquor evaporation system. One is condensate from the forced circulation concentrator. These rarely contributed more than about 400 liters per metric ton of pulp production (100 gal/ton) to the total mill effluent and represent condensate obtained from the last stage of liquor concentration. Concentrators normally increase the liquor solids from about 50 to 65 percent.

Seven samples were obtained from three mills and four different forced-circulation concentrators. These sources included: (a) mill B number 2 concentrator, (b) mill D number 2 concentrator, and (c) mill I concentrator surface condenser condensate and, (d) mill I concentrator condensate.

The identifiable odor thresholds of all four of these process streams were low and similar ranging from 3.7×10^4 to 8.5×10^4. The log average of these twelve samples was 5.1×10^4 as shown in Table 19.

Black Liquor Multiple-Effect Evaporator Total Condensate

The combined multiple-effect evaporator condensate stream had an average flow of 5,400 to 10,200 liters/metric ton (1,300 to 2,500 gal/ton or 520 to 750 gla/1,000 lbs of black liquor solids). Sixteen samples of the combined multiple-effect evaporator condensates were obtained from five different mills for odor threshold analysis. The results indicated that the identifiable odor thrshold varied from 1.4×10^5 to 3.1×10^7 with a log average of 2.5×10^6. These results are shown in Table 20.

Run 4 was not included in the general data summary as that sample was obtained during a period of multiple-effect evaporator boil-out. The high conductivity observed in that sample was of some note, since it was a factor of almost 20 greater than the conductivity of other similar samples measured during this study.

The odor values obtained on condensates from mills A and B were somewhat higher than those reported for the other mills, a log average of the identifiable odor threshold of 1.1×10^7 as compared to 1.9×10^6. When comparing the sample value ranges, the Southern mills A and B, varied from 3.8×10^6 to 2.2×10^7, whereas the West Coast mills varied from 4.3×10^5 to 3.1×10^7. The conductivity values did not indicate a difference in liquor carryover. The difference may have been due to the difference in wood species pulped.

TABLE 19. IDENTIFIABLE ODOR THRESHOLD OF FORCED CIRCULATION CONCENTRATOR CONDENSATES

Run	Mill ident.	Source	No. of panel.	No. of panelists ident. odor at all dil.	Maximum test dilution $(x10^{-5})$	ED_{50} dilution factor $(x10^{-5})$	No. of panelists "missed low"	Min. Dil. at level missed $(x10^{-5})$
1	B	#2 Conc. evap.	6	0	-	0.56	1	0.058
2	B*	#2 Conc. evap.	8	0	-	0.24	0	-
3	D	#2 Conc. cond.	8	0	-	0.44	1	0.058
4	D*	#2 Conc. cond.	8	0	-	1.2	0	-
5	D	#2 Conc. cond.	7	1	8.4	1.0	0	-
6	I	Conc. S.C. cond.	8	0	-	0.21	0	-
7	I	Conc. S.C. cond.	8	0	-	1.2	0	-
8	I*	Conc. S.C. cond.	8	0	-	<0.81	2	0.12
9	I	Conc. cond.	8	0	-	1.8	0	-
10	I*	Conc. cond.	8	0	-	0.85	0	-
11	I	Conc. cond.	8	0	-	0.12	0	-
12	I*	Conc. cond.	8	0	-	0.16	0	-
				Log average (all sources)		0.51		

* Duplicate sample, only log average of duplicates utilized in mill log average

TABLE 20. IDENTIFIABLE ODOR THRESHOLD OF COMBINED MULTIPLE-EFFECT EVAPORATOR CONDENSATES

Run	Mill ident.	No. of panelists	No. of panelists ident. odor at all dil.	Maximum test dilution ($x10^{-5}$)	ED_{50} dilution factor ($x10^{-5}$)	No. of panelists "missed low"	Min. dil. at level missed ($x10^{-5}$)	Conductivity (mhos/cm)
1	A	7	1	4200	220	0	-	270
2	B	6	0	-	<83	0	12	240
3	B*	7	0	-	38	0	-	
4	C+	7	0	-	0.45	1	0.058	~7000
5	C	6	0	-	4.7	0	-	390
6	C	5	0	8.4	>4.3	0	-	260
7	C	9	0	-	4.4	0	-	260
8	C	7	0	-	4.3	0	-	350
9	C	6	0	-	89	0	-	-
10	C	6	0	-	310	0	-	-
11	C	7	0	-	43	1	5.8	-
		Log average mill C			>17			
12	D	8	1	84	6.2	0	-	330
13	D	7	0	-	1.4	0	-	430
14	E	8	2	42	>10	0	-	485
15	E	8	1	420	55	0	-	290
16	E	7	0	-	12	0	-	200
17	E	7	0	-	5.4	0	-	255
		Log average mill E			14			
		Log average, all mills			24			

* Duplicate sample (same sample, same day) only log average of duplicates utilized in mill log average

+ Multiple-effect evaporator on boil-out, not included in mill log average

TABLE 21. IDENTIFIABLE ODOR THRESHOLD OF MULTIPLE-EFFECT EVAPORATOR CONDENSATES FROM MILL A

Run	Source	No. of panelists	No. of panelists ident. odor at all dil.	Maximum test dilution $(x10^{-5})$	ED_{50} dilution factor $(x10^{-5})$	No. of panelists "missed low"	Min. dil. at level missed $(x10^{-5})$	Cond. (μ mhos/cm)
1	#1 MEE & Conc. comb. cond.	7	3	0.011	0.00070	1	0.000014	10
2	#2 Body cond.	7	0	-	13	3	5.8	300
3	#3 Body cond.*	7	0	-	16	3	5.8	
4	#3 Body cond.	7	0	-	3.7	1	0.58	310
5	MEE hot well	7	0	-	610	1	230	40
6	MEE comb. cond.	7	0	-	220	1	4200	270

* Duplicate of previous run (same sample, same day)

TABLE 22. IDENTIFIABLE ODOR THRESHOLD OF MULTIPLE-EFFECT EVAPORATOR CONDENSATES FROM MILL B

Run	Source	No. of panelists	No. of panelists ident. odor at all dil.	Maximum test dilution $(x10^{-5})$	ED_{50} dilution factor $(x10^{-5})$	No. of panelists "missed low"	Min. dil. at level missed $(x10^{-5})$	Cond. (mhos/cm)	Flow (gpm)
1	#2 Conc. +	6	1	1.1	0.089	0	-	n.d.$^{+}$	
2	2,3,4,5 MEE	8*	0	-	0.58	1	0.058		
3	Hot well	6	0	-	690	2	120	410	
4	(#6 vapors)	7*	0	-	510	0	-		
5	Comb. MEE cond.	6	0	-	83	2	12	240	460
6		8*	0	-	38	0	-		

* Duplicate of previous run, collected simultaneously but analyzed for odor threshold on different days

+ n.d. denotes not detectable

TABLE 23. IDENTIFIABLE ODOR THRESHOLD OF MULTIPLE-EFFECT EVAPORATOR CONDENSATES FROM MILL C

Run	Source	No. of panelists	No. of panelists ident. odor at all dil.	Maximum test dilution ($x10^{-5}$)	ED_{50} dilution factor ($x10^{-5}$)	No. of panelists "missed low"	Min. dil. at level missed ($x10^{-5}$)	Cond. (μmhos/cm)	Approx. flow (gpm)
1	#3 Body cond.	7	0	-	0.021	0	-	-	62
2		7	0	-	0.017	0	-	-	
3		6	0	-	0.040	0	-	25	
4		6	1	0.42	0.067	0	-	15	
	Log average #3 body condensate				0.031				
5	#4 Body cond.	6	0	-	0.023	0	-	85	147
6		6	1	0.42	0.095	0	-	-	
7	#5 Body cond.	6	-	-	0.12	0	-	25	272
8		6	1	0.42	0.14	0	-	-	
9	#6 Body cond.	6	0	-	0.46	0	-	130	412
10		6	0	-	0.83	0	-	20	
11	#7 Body cond.	6	0	-	0.13	0	-	125	497
12		6	3	0.21	0.076	0	-	20	
13	S.C. cond.*	-			18				
14	S.C. cond.*	-			18				
15	S.C. cond.*	-			<25			1550	123
16	S.C. cond.*	-			2.2			1650	
17	S.C. cond.	6	0	-	12	0	-	1475	
18	S.C. cond.	6	0	-	5.9	0	-	975	
	Log average S.C. condensate				<10				
19	Comb. cond.	7+	0	-	0.45	1	0.058	~7000	620
20		6	0	-	4.7	0	-	390	
21		5	2	8.4	>4.3	0	-	260	
22		9	0	-	4.4	0	-		
23		7	0	-	4.3	0	-		
24		6	0	-	89	0	-		
25		7	0	-	43	0	-		
26		7	0	-	43	0	-		
	Log average combined condensate				>11				

* Log average of daily results, 2 to 8 tests per day

+ Multiple-effect evaporator on boil-out, not included in source log average

Components of Multiple-Effect Evaporator Condensates

Condensate samples were collected at five different locations around the multiple-effect evaporators at the Southeastern mill A. At this location a split liquor feed to bodies 4 and 5 was featured. The samples included the number 1 multiple-effect evaporator condensate mixed with the combined concentrator condensates, the number 2 multiple-effect evaporator body condensate, the number 3 body condensate, the multiple-effect evaporator hot well, and the combined multiple-effect evaporator condensate which also contained the surface condenser condensate. The results from these samples, as shown in Table 21, indicated that the largest portion of the odor could be attributed to those condensates originating from the first stages of liquor evaporation. The identifiable odor threshold of the condensate through the third body was only 3.7×10^5. Addition of those condensates from the fourth and fifth bodies increased the identifiable odor threshold to 6.1×10^7.

Mill B featured a mid-body liquor feed. The liquor entered body no. 5 and flowed sequentially to bodies 6, 4, 3, 2, and 1. Condensate samples were collected from three different locations in this multiple-effect evaporator system. The three samples included one containing the number 2 concentrator and numbers 2, 3, 4, and 5 multiple-effect evaporator condensate, one from the evaporator hot well which included the vapors from the number 6 body, and one containing the combined condensates from the total black liquor evaporation system. The data, as shown in Table 22, indicated that the condensates from the later stages of evaporation had a minimal identifiable odor threshold when compared to those originating from the first stages of evaporation. Attention is called to the data for runs 1 and 2 as compared to runs 3 and 4. The results indicated that the number 6 evaporator body condensate had an identifiable odor threshold of 5×10^7, whereas those condensates from the latter stages of evaporation had an identifiable odor threshold of 6.0×10^4.

The multiple-effect evaporators at mill C were operated in a strictly counter-current flow manner with liquor feed to body 7 and continuing sequentially to 6, 5, 4, 3, 2, and 1. Samples were collected from this system at number 3 evaporator body, number 4 evaporator body, number 5 evaporator body, number 6 evaporator body, number 7 evaporator body, the surface condenser, and the combined multiple-effect evaporator and concentrator condensates.

The results presented in Table 23 indicate that the primary odor contribution was from the vapors off the number 7 evaporator body. These vapors were condensed and emerged as condensates from the surface condenser which had an identifiable odor threshold log average of 1.0×10^6 with variations between 2.2×10^5 and about 2.5×10^6. The converse was also true, those condensates from the bodies at the latter end of the liquor evaporation sequence contained much lower identifiable odor thresholds as exemplified by the number 3 multiple-effect evaporator body condensates. This body had a log average identifiable odor threshold of 3.1×10^4 with a range of 1.7×10^4 to 6.7×10^4.

Multiple-effect evaporator condensate samples were also obtained from mill D. These multiple-effect evaporators were mid-feed units. The feed was to the 4th effect and then the liquor progressed sequentially to the 5th, 3rd, 2nd, and 1st effect prior to entering the concentrators. Samples were collected from five different locations in this complex including the number 2 evaporator body, the number 4 evaporator body, the number 5 evaporator body, the surface condenser and the hot well which contained the combined evaporator condensates.

The results, as shown in Table 24, indicated that the first stages of liquor evaporation had the highest identifiable odor threshold dilution level. This was exemplified in the values obtained from the surface condenser condensates which varied from 1.2×10^6 to 4.5×10^6. Additionally, those condensates from the latter stages of evaporation had lower identifiable odor thresholds as shown by the data obtained from the number 2 body and number 4 body condensates. The number 2 body condensate threshold varied from 6.9×10^4 to 2.1×10^5 and the number 4 body condensates varied from 1.8×10^4 to 1.3×10^5.

Multiple-effect evaporator condensates were analyzed from mill E and the data is presented in Table 25. At this location the liquor feed was split to the evaporators. The liquor entered bodies 5 and 6 concurrently, then recombined and sequentially entered bodies 4, 3, 2, and 1. Samples were collected from six different locations at this mill, including the number 2 body condensate, the number 3 body condensate, the number 4 body condensate, the number 5 body condensate, the number 6 body condensate, and the evaporator hot well which was the total evaporator condensates.

This set of samples did not follow the expected odor intensity pattern as clearly as at the previous locations. In an attempt to understand what may have happened, the conductivity of the condensates are also presented in the table. The conductivities increased as a trend toward the liquor feed end, but not significantly. They did not explain the difference in behavior of this set of samples when compared to the others. This information points to the need to evaluate each source independently. The identifiable odor thresholds at the number 2 body varied from 1.8×10^5 to 2.7×10^5. This increased for the hot well condensates where the identifiable odor threshold varied from $>1 \times 10^6$ to 5.5×10^6.

TABLE 24. IDENTIFIABLE ODOR THRESHOLD OF MULTIPLE-EFFECT EVAPORATOR CONDENSATES FROM MILL D

Run	Source	No. of panelists	No. of panelists ident. odor at all dil.	Maximum test dilution $(x10^{-5})$	ED_{50} dilution factor $(x10^{-5})$	No. of panelists "missed low"	Min. dil. at level missed $(x10^{-5})$	Cond. (μmhos/cm)	Flow (gpm)
1	#2 Body cond.	8	0	-	0.87	0	-	320	168
2		8*	0	-	0.69	0	-		
3		7	0	-	0.89	0	-	235	
4		7*	0	-	2.1	0	-		
5	#4 Body cond.	8	0	-	0.18	0	-	400	560
6		7	0	-	0.89	0	-	820	
7		7*	0	-	1.3	0	-		
8	#5 Body cond.	8	0	-	0.94	0	-	440	716
9		7	0	-	1.0	0	-	1150	
10	S.C. cond.	8	0	-	12	0	-	360	158
11		7	1	840	45	0	-	250	
12	Hot well (comb. cond.)	8	1	84	6.2	0	-	330	946
13		7	0	-	1.4	0	-	430	

* Duplicate of previous run (same sample, same day)

TABLE 25. IDENTIFIABLE ODOR THRESHOLD OF MULTIPLE-EFFECT EVAPORATOR CONDENSATES FROM MILL E

Run	Source	No. of panelists	No. of panelists ident. odor at all dil.	Maximum test dilution ($x10^{-5}$)	ED_{50} dilution factor ($x10^{-5}$)	No. of panelists "missed low"	Min. dil. at level missed ($x10^{-5}$)	Cond. (μmhos/cm)	Flow (gpm)
1	#2 Body cond.	8	0	-	2.2	0	-	32	164
2		8*	0	-	2.7	0	-		
3		8	0	-	1.8	2	0.58	40	
4	#3 Body cond.	8	0	-	3.4	0	-	42	318
5		8	0	-	3.2	0	-	25	
6	#4 Body cond.	8	1	4.2	1.4	0	-	100	408
7		8	1	42	3.1	0	-	65	
8	#5 Body cond.	8	0	-	0.36	0	-	120	576
9		8	1	4.2	1.1	0	-	135	
10	#6 Body cond.	8	1	420	31	0	-	95	642
11		8	1	8.4	0.90	0	-	100	
12	Hot well (comb. cond.)	8	2	42	10	0	-	485	829
13		8	1	840	55	0	-	290	

* Duplicate of previous run (same sample, same day)

TABLE 26. IDENTIFIABLE ODOR THRESHOLD OF MULTIPLE-EFFECT EVAPORATOR CONDENSATES FROM MILL I

Run	Source	No. of panelists	No. of panelists ident. odor at all dil.	Maximum test dilution $(x10^{-5})$	ED_{50} dilution factor $(x10^{-5})$	No. of panelists "missed low"	Min. dil. at level missed $(x10^{-5})$	Cond. (μmhos/cm)	Flow (gpm)
1	#3 Body cond.	7	0	-	0.024	0	-	n.d.	110
2	#4 Body cond.	8	1	0.21	0.039	0	-	-	258
3		7	0	-	0.047	0	-	25	
4	#5 Body cond.	8	2	0.42	0.11	0	-	-	366
5		7	0	-	0.028	0	-	110	
6	#6 Body cond.	8	0	-	0.047	0	-	-	537
7		7	-	-	0.18	0	-	230	
8	#7 Body cond.	8	2	0.42	0.010	0	-	-	656
9		7	0	-	0.14	0	-	60	
10	S.C. cond.	8	0	-	2.1	0	-	-	116
11		7	0	-	7.8	0	-	315	

* n.d. denotes not detectable

The last multiple-effect evaporator complex investigated was that at mill I which featured a split liquor feed to the 6th and 7th effects with the flow continuing sequentially, to numbers 5, 4, 3, 2, and 1 effects. Samples were collected from six different sources for analysis, including the number 3 body, the number 4 body, the number 5 body, the number 6 body, the number 7 body, and the surface condenser condensate.

These samples, with the exception of number 7 body condensates, very nicely follow the progression of identifiable odor thresholds experienced with previous samples. The results are presented in Table 26. The Ed_{50} of the number 3 multiple-effect evaporator body condensate was the lowest. The two samples gave values of $2.4x10^3$ and $>3.2x10^3$. The highest odor threshold values were from the surface condenser condensates and the two samples gave values of $2.1x10^5$ and $7.8x10^5$. It was noted that the condensate from the number 7 body had a lower identifiable odor threshold than that from number 6 body. It was determined that the lower ED_{50} was caused by lesser liquor carryover, since the conductivity of the condensate from the number 7 body was also lower than that from number 6.

By carefully observing Tables 21-26, it can be seen that the vapors from the first two liquor stages of evaporation required more dilution to reach the identifiable odor threshold. This is in agreement with previous findings that indicated most of the volatile constitutents in black liquor were removed in the first few stages of the multiple-effect evaporators (62).

Digester Condensates

The identifiable odor threshold of the digester condensate streams varied as a function of the condensation method utilized. At mill C, indirect heat exchangers for condensation were used, whereas at the other four locations sampled, direct or jet condensers were utilized to reduce the temperature of the digester blow gas prior to treatment.

At mill C, the identifiable odor threshold of the digester condensates had a log average of $2.9x10^7$ as shown in Table 27, and ranged from $7.0x10^6$ to $>1.4x10^8$. The other four locations used direct condensation for gas stream temperature control and the condensates had a log average identifiable odor threshold of $4.8x10^5$ and a range of $3.1x10^4$ to $3.7x10^7$.

It was apparent that the direct contact condensers, with the resultant dilution water yielded condensates with an average identifiable odor threshold that was lower than those from indirect condensers. It was assumed that the difference in identifiable odor threshold observed for the direct contact condensates was due to the dilution provided. The effluent volume associated with direct condensers is variable and a function of the

TABLE 27. IDENTIFIABLE ODOR THRESHOLDS OF DIGESTER CONDENSATES

Run	Mill ident.	No. of panel.	No. of panelists ident. odor at all dil.	Maximum test dilution $(x10^{-5})$	ED_{50} dilution factor $(x10^{-5})$	No. of panelists "missed low"	Min. dil. at level missed $(x10^{-5})$
1	A	7	2	84	1.6	2	0.12
2	A	7	0	-	3.0	0	-
3	B	7	0	-	11	0	-
4	C*	7	0	-	110	0	-
5	C*	6	0	-	70	1	12
6	C*	9	0	-	480	0	-
7	C*	6	1	4200	550	0	-
8	C*	6	2	8400	>1400	0	-
9	C*	7	0	-	200	0	-
10	F	7	0	-	7.8	0	-
11	F	6	0	-	365	0	-
12	G	6	0	-	2.5	0	-
13	G	6	1	84	7.6	0	-
14	G	7	0	-	1.4	0	-
15	G	7	0	-	0.31	0	-
			Log average		24		

* Indirect condenser

individual design. Effluent flows associated with indirect condensers are on the order of 1.3 liter/minute (0.35 gal/min) per ton of production.

First Chlorination Stage Bleach Plant Effluent

The first chlorination stage effluent from the bleach plant had a relatively low identifiable odor threshold. Seven runs were performed on six different samples from three different mills and the data is shown in Table 28. The log average of the identifiable odor threshold was 1.2×10^3 with a range of 8.1×10^1 to 1.4×10^5.

The information generated in other portions of this study is of significance when interpreting the information on the relative odor threshold level of this process stream. When the odor threshold levels were determined for the individual components of these combined streams and a combined odor threshold calculated it was found somewhat, if marginally, greater than the odor threshold of the actual combined stream. For example, the odor threshold levels of the actual combined streams were 0.11×10^5, 1.1×10^5, and 5.6×10^5 while the calculated odor thresholds were 15×10^5, 2.5×10^5, and 2.3×10^5 respectively as shown in Table 33. These data indicate that there was some benefit in mixing these odorous streams with the bleach plant effluent.

The run 7 sample from mill C appeared to be an anomaly with no reason apparent for the high value of 1.4×10^5 reported. This value was 2 orders of magnitude greater than other odor thresholds found from this source during the study.

It was noted that the odor perceived in the flask at the identifiable odor threshold level for all bleach plant effluent samples had a different characteristic than the previewed odor. The characteristic chlorine odor of the concentrated sample was not the odor perceived at the identifiable odor threshold level by the panelists. These observations indicated that the chlorine odor was not significant or predominant at the threshold level.

Mixtures of First Chlorination Stage Effluent and Digester and Evaporator Condensates

It was estimated that about 29,200 liters/metric ton (7,000 gal/ton) of flow could be attributed to first stage chlorination effluents. This flow is mixed with that from the multiple-effect evaporators and the digester condensates at some mills. The flow from these two sewers is on the order of 10,000-11,000 liters/metric ton (2000-2500 gal/ton). The purpose of mixing is to permit the residual chlorine in the bleach plant effluent to react with sulfides and other odor causing constituents of the

TABLE 28. IDENTIFIABLE ODOR THRESHOLD OF 1ST CHLORINATION STAGE FILTRATE

Run	Mill ident.	No. of panel.	No. of panelists ident. odor at all dil.	Maximum test dilution ($x10^{-5}$)	ED_{50} dilution factor ($x10^{-5}$)	No. of panelists "missed low"	Min. dil. at level missed ($x10^{-5}$)
1	B	8	0	-	<0.0037	2	0.000015
2	C	7	0	-	<0.0038	3	0.0017
3	C	6	0	-	0.00081	0	-
4	C*	6	0	-	0.0011	0	-
5	C	9	0	-	0.013	0	-
6	C	7	0	-	0.013	1	0.00029
7	C	6	1	4.2	1.4	0	-
			Log average		0.012		

* Duplicate of previous run (same sample, same day) combination counted as one run in log average

condensate streams in an effort to reduce the odor attributable to these effluents.

At one location, mill C, mixing of the above process streams was normal operation. Eleven odor determinations were made on ten samples from this combined stream. One of these samples was collected while the multiple-effect evaporators were operated in the boil-out mode as is shown in Table 29. The identifiable odor threshold log average for these combined streams was $4.5\text{x}10^6$ with a range of $1.1\text{x}10^4$ to $1.0\text{x}10^7$. This compared with a log average of $1.0\text{x}10^3$ and a range of $8.1\text{x}10^1$ to $1.4\text{x}10^5$ for just the first chlorination stage bleach plant effluent from this mill, an increase of more than two orders of magnitude.

TABLE 29. IDENTIFIABLE ODOR THRESHOLD OF BLEACH PLANT ACID SEWER COMBINED WITH CONDENSATES FROM MEE AND DIGESTERS AT MILL C

Run	No. of panel.	No. of panelists ident. odor at all dil.	Maximum test dilution ($\text{x}10^{-5}$)	ED_{50} dilution factor ($\text{x}10^{-5}$)	No. of panel. "missed low"	Min. dil. at level missed ($\text{x}10^{-5}$)
1*	7	0	-	0.20	0	-
2	6	0	-	11	0	-
3+	6	0	-	4.7	0	-
4	8	0	-	4.1	0	-
5	6	1	840	100	0	-
6	7	0	-	4.5	0	-
7	9	2	4.2	0.11	0	-
8	7	1	42	1.1	0	-
9	6	1	42	5.6	0	-
10	6	0	-	6.5	0	-
11	7	0	-	12	1	1.2
	Log average			4.5		

* MEE on boil-out, not included in average

+ Duplicate of previous run (same sample, same day), log average of both runs used in log average

Steam and Air Stripper Streams

Six determinations and one duplicate were made on stripper feeds from three different locations. The results are shown in Table 30.

The feed to the three systems studied was quite varied and included such sources as turpentine decanter underflows, digester condensates and multiple-effect evaporator condensates. The identifiable odor thresholds of these feeds had a log average of $3.8\text{x}10^6$ with a range from $2.0\text{x}10^5$ to $3.5\text{x}10^7$.

TABLE 30. IDENTIFIABLE ODOR THRESHOLD OF STRIPPER FEED

Run	Mill ident.	No. of panel.	No. of panelists ident. odor at all dil.	Maximum test dilution ($x10^{-5}$)	ED_{50} dilution factor ($x10^{-5}$)	No. of panelists "missed low"	Min. dil. at level missed ($x10^{-5}$)
1	F	7	0	-	350	1	120
2	F*	7	0	-	300	1	120
3	F	6	0	-	160	0	-
4	H+	6	0	-	146	0	-
5	H+	6	0	-	<24	3	12
6	I	8	0	-	2.0	0	-
7	I	7	0	-	7.8	0	-
			Log average		38		

* Duplicate of previous run (same sample, same day), log average used in column log average

+ Feed to air stripper

The stripper feed at mill F was the multiple-effect evaporator surface condenser condensates, the turpentine decanter underflow and the vapor compression evaporator vent condensates at about 2700 liters/metric ton (650 gal/ton). At mill H the stripper feed included the turpentine decanter underflow and condensate from the number 5 body of a five body mid-feed multiple-effect evaporator set for a total flow of about 1600 liters/metric ton (about 400 gal/ton). At mill I the feed to the stripper included turpentine decanter underflow, stripper vacuum pump seal water, concentrator and evaporator surface condenser condensates and vapor compression evaporator condensates for a total flow of about 1300 liters/metric ton (300 gal/ton). These were typical of some of the most odorous streams identified.

Six determinations were made on air and steam stripped materials from three different mills and the data is presented in Table 31. The sample from mill H followed an air stripper, whereas the other four samples followed steam strippers. This air stripper was a temporary installation that received about 190 liters/minute (50 gpm) of feed condensate and about 22.7 m^3/min (800 cfm) of air. The air to liquid feed ratio was about 40 to 1. Odor threshold reduction across the air stripper was about 50 percent. Since this was a temporary unit, it is suspected that the unit was not optimized and these results may not have been representative of the capability of these systems.

Table 31 indicated the identifiable odor threshold of the product from the two steam strippers had a log average of $1.4x10^3$ to $2.8x10^4$. The odor thresholds of the bottoms from the steam strippers at both sites were similar despite the difference in the feed odor thresholds. This indicated that the odorous constituents in the effluent streams that were removable by steam stripping had been volatilized.

SUMMARY OF PROCESS STREAM IDENTIFIABLE ODOR THRESHOLDS

The range and/or log averages of the identifiable odor thresholds have been summarized and presented in Table 32. These values indicate that the most odoriferous streams, as a class, were those that were termed in-process liquor steams with a high pH and high sodium sulfide content. These included white liquor, black liquor, weak wash, and green liquor. Excluding the weak black liquor samples, these streams had a combined log average identifiable odor threshold of $2.0x10^7$ with the highest being a green liquor measurement at $6.3x10^8$ and the lowest being another green liquor sample at $2.6x10^6$.

The various condensate streams originating from handling black liquor had the next highest identifiable odor thresholds, having a combined log average of $3.2x10^6$. The streams included in this classification were the turpentine decanter underflow,

TABLE 31. IDENTIFIABLE ODOR THRESHOLD OF AIR AND STEAM STRIPPED MATERIAL

Run	Mill ident.	No. of panel.	No. of panelists ident. odor at all dil.	Maximum test dilution ($x10^{-5}$)	ED_{50} dilution factor ($x10^{-5}$)	No. of panelists "missed low"	Min. dil. at level missed ($x10^{-5}$)
1	F	7	1	4.2	0.28	0	-
2	F	6	0	-	0.18	0	-
3	H*	6	0	-	60	1	12
4	H*	6	0	-	35	3	12
5	I	7	0	-	0.12	0	-
6	I	7	0	-	0.072	0	-
		Log average			0.14		

* Air stripper material not included in column log average

TABLE 32. SUMMARY OF IDENTIFIABLE ODOR THRESHOLDS FOR SOURCES EVALUATED

Source	No. of trails*	ED_{50} ($x10^{-5}$) Maximum	Log average	Minimum
Non-cond. line condensate	2	11000	-	1100
White liquor	2	410	-	195
Weak wash	2	400	-	90
Green liquor	3	630	-	<26
Black liquor	2	0.31	-	0.010
Turpentine decanter underflow	10	>1200	72	2.9
Air stripper product	2	60	-	<35
Stripper feed	6	350	38	2.0
VCE (VRE) vapor condensates	6	712	30	3.3
MEE combined condensate	15	310	24	1.4
Digester condensate	15	>1400	24	0.31
Decker filtrate after pulp cleaners	7	42	0.84	0.0078
Steam stripper product	4	0.28	0.14	0.072
1st chlorination stage filtrate	7	13	0.012	0.00081

* Duplicate runs on same sample indicated as one trial

+ Temporary unit, not optimized

the vacuum compression evaporator condensates, the digester condensates, and the multiple-effect evaporator condensates, in descending order with respect to identifiable odor thresholds.

Process streams with low dilution ratios to the threshold level and being within a factor of ten of each other included the decker filtrates, the brown stock washer filtrates, the steam stripper product, and chlorination stage filtrates.

ADDITIVE NATURE OF EFFLUENTS (ODOR BALANCE)

An effort was made to determine if odor thresholds of various process streams were additive or could be simulated. While it was established that odor thresholds of these effluent samples could not be predicted from the reduced sulfur analysis, the odor threshold may be additive. If odor thresholds are additive, it would be possible to predict the impact of a process change on total effluent odor threshold. Seven trials were run including five designed to simulate bleach plant effluent that received digester and multiple-effect evaporator condensates. Two trials were run to simulate a total unbleached kraft mill effluent.

The first three runs, as shown in Table 33, were performed to investigate the effects of various modes of sample mixing on the identifiable odor threshold. Those samples designated "Synthetic I" were made by adding 15 mls of chlorination stage bleach plant effluent, 1 ml of multiple-effect evaporator combined condensates, and 0.5 ml of digester condensates, individually to the odor-free water. This solution was then sequentially diluted as necessary. Those samples designated as "Synthetic II" were made by diluting the chlorination stage effluent, the multiple-effect evaporator combined condensates, and the digester condensates, individually to 2000:1 prior to mixing together in the proportions as required to become the stock solution. Those identified by "Synthetic III" were prepared by adding 30 ml of chlorination stage effluent to 2 ml of multiple-effect evaporator combined condensate and 1 ml of digester condensate, and then transferring 1 ml of this solution to the first dilution stage of 2000 ml. This sample was then sequentially diluted as necessary.

In the first two sets of data all three dilution techniques Synthetic I, II, and III, appeared to give similar results. However, in the third set of data the results appeared to be incongruous with the previous information. There was no identifiable reason for the discrepancy noted in the third run.

For the fourth and fifth data sets, digester and multiple-effect evaporator condensate were diluted in odor free water. The purpose was two-fold, (a) to investigate the ability to simulate a complex process stream by adding only the compounds of major impact to the identifiable odor threshold, and (b) to determine the effect of the chlorine on the identifiable odor

TABLE 33. ADDITIVE NATURE OF ODOR FROM MILL PROCESS STREAMS

Data set	Run	Source	No. of panel.	No. of panelists ident. odor at all dil.	Maximum test dilution ($x10^{-5}$)	ED_{50} dilution factor ($x10^{-5}$)	No. of panelists "missed low"	Min. dil. at level missed ($x10^{-5}$)
I	1	MEE comb. cond.	9	0	-	4.4	0	-
	2	Cl_2 stage filtrate	9	0	-	0.013	0	-
	3	Dig. cond.	9	0	-	480	0	-
	4	Acid sewer	9	2	4.2	0.11	0	-
	5	Synthetic I^1	9	0	-	6.7	0	-
	6	Synthetic II^2	9	0	-	16	0	-
	7	Synthetic III^3	9	0	-	<1.4	5	0.58
		Calculated^6				15		
II	8	MEE comb. cond.	7	0	-	4.3	-	-
	9	Cl_2 stage filtrate	7	0	-	0.013	1	0.00029
	10	Dig. cond.	7	0	-	>72	3	12
	11	Acid sewer	7	1	42	1.1	0	-
	12	Synthetic I^1	7	1	51	3.4	0	-
	13	Synthetic II^2	7	0	-	3.5	0	-
	14	Synthetic III^3	7	0	-	3.1	0	-
		Calculated^6				2.5		
III	15	MEE comb. cond.	6	2	420	89	0	-
	16	Cl_2 stage filtrate	6	1	4.2	1.4	0	-
	17	Dig. cond.	6	1	4200	550	0	-
	18	Acid sewer	6	1	42	5.6	0	-
	19	Synthetic^1	6	2	51000	> 7500	0	-
	20	Synthetic III^3	6	1	84000	2400	1	120
		Calculated^6				23		
IV	21	MEE comb. cond.	6	0	-	310	0	-
	22	Dig. cond	6	2	8400	> 1400	0	-
	23	Simulated acid sewer^4	6	1	840	50	0	-

(continued)

TABLE 33. (Continued)

Data Set	Run	Source	No. of panel.	No. of panelists ident. odor at all dil.	Maximum test dilution ($x10^{-5}$)	ED_{50} dilution factor ($x10^{-5}$)	No. of panelists "missed low"	Min. Dil. at level missed ($x10^{-5}$)
V	24	MEE comb. cond.	7	0	-	43	1	5.8
	25	Dig. cond.	7	0	-	200	0	-
	26	Simulated acid sewer[4]	7	0	-	31	0	-
		Calculated[6]				23		
VI	27	Decker water	7	0	-	18	1	0.58
	28	MEE & conc. hot well	7	0	-	5.4	0	-
	29	Total mill effluent	7	0	-	16	0	-
	30	Simulated TME[5]	7	0	-	2.8	1	-
		Calculated[6]				7.2		

1. Made by adding 15 ml Cl_2 stage effluent, 1 ml MEE comb. cond., and 0.5 ml dig. cond. to first dilution stage water.
2. Made by diluting Cl_2 stage effluent, MEE comb. cond. and dig. cond. 2000:1, then adding 150 ml Cl_2 stage, 10 ml MEE comb. cond., and 5 ml dig. cond. dilute solutions to first dilution stage water.
3. Made by combining 30 ml Cl_2 stage, 2 ml MEE comb. cond., and 1 ml dig. cond., then 1 ml taken for first dilution stage.
4. Made by combining 17.1 ml H_2O (rather than Cl_2 stage filtrate), 6.4 ml MEE comb. cond., and 1.5 ml dig. cond., then 1 ml taken for first dilution stage.
5. Made by combining 5 ml H_2), 1.3 ml MEE cond., and 3.7 ml decker water, then 1 ml taken for first dilution stage.
6. Calculated threshold from determined odor level of constituents and volume of each used in process.

thresholds. The results indicated that the calculated and diluted odor thresholds were the same number. This showed that the effects of dilution on condensate streams could be calculated.

A test was also performed on a simulated total unbleached kraft mill effluent. This run was performed by combining screen room decker filtrate, multiple-effect evaporator and concentrator combined condensate with odor-free water in the proper proportions to simulate the total mill effluent. In this instance, 5 ml of odor free water, 1.3 ml of evaporator and concentrator condensates, and 3.7 ml of screen room decker filtrate were combined. The results are presented as data set VI and indicated that the impact of an odorous effluent from the kraft pulping process on the total mill effluent odor threshold could be calculated.

The calculated "identifiable" odor thresholds presented for each set of data was calculated in the manner shown in the following example:

For Data Set I

One volume of multiple-effect evaporator condensates at an "IOT" of $4.4x10^5$ and one-half volume of digester condensates at an "IOT" of $480x10^5$ in fifteen volumes of first chlorination stage bleach plant effluent at an "IOT" of $0.13x10^5$

$$\frac{1x(4.4x10^5) + 0.5x(480x10^5) + 15x(0.13x10^5)}{(1 + 0.5 + 15)} \quad 15x10^5$$

SUMMARY

The data generated in this portion of the study indicated that within the limits of the test procedure, the identifiable odor threshold associated with effluents from kraft pulping process streams can be determined and duplicated using head space analysis for the identifiable odor and the triangle testing technique. The work also showed that the effect of one process stream on the total mill effluent odor level could be simulated using a weighted average calculation.

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